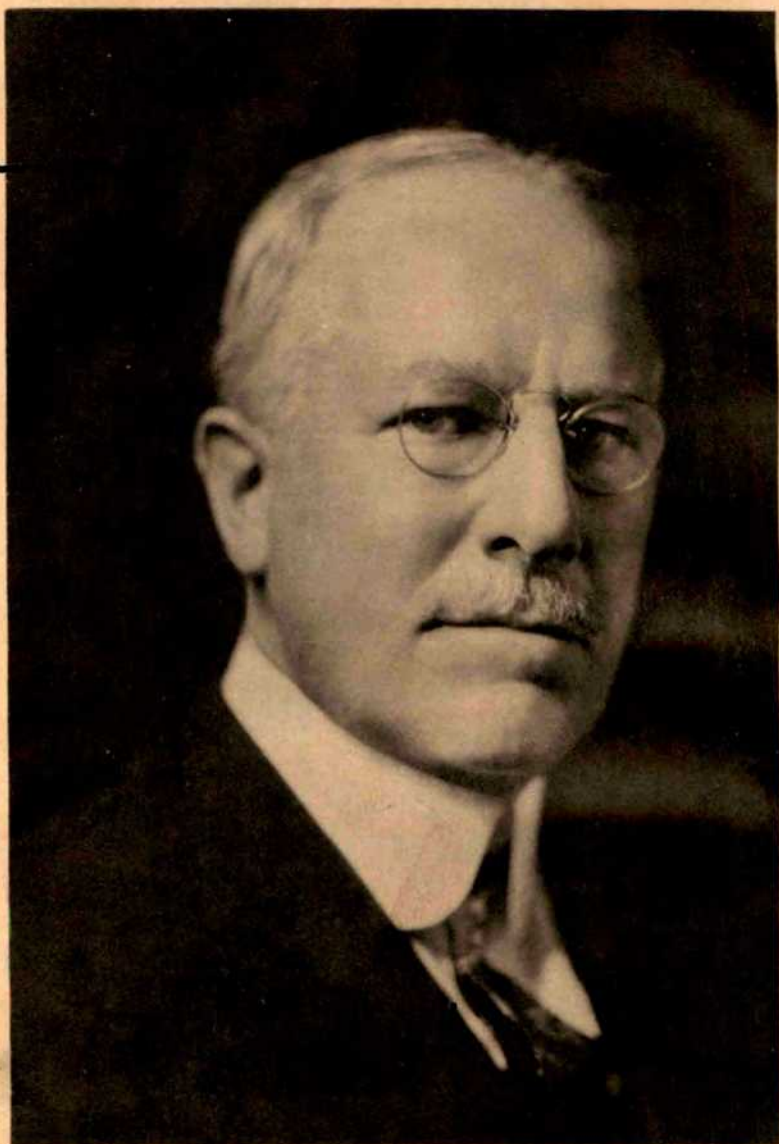


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Arthur R. Day

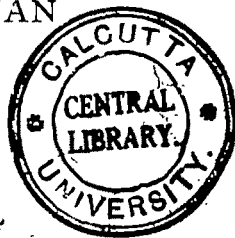
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Carnegie Institution of Washington

Publication No. 1000

DEDICATED TO
ARTHUR LOUIS DAY
IN GRATEFUL APPRECIATION
BY THE AUTHORS



"It has been found thoroughly practicable to study several of the important problems in mineral formation by applying the principles and methods of physics and physical chemistry at the temperature where the formation actually occurs, and to carry out the quantitative determinations with an accuracy entirely comparable with the more conventional physical and chemical research at ordinary temperatures * * *.

"The essential novelty of the present plan, when freed from all technical terms and expressions, is this: It has been the habit heretofore, in investigating the makeup of the earth, either to study natural minerals in which, of course, the formation process is already complete and no longer accessible, or to study artificial minerals in the same way after actual formation is over. Our plan has been to transfer the investigation as far as possible to the region where the earth-making processes are at work, and to observe the minerals during actual formation. Only in this way, in my opinion, can we succeed in ascertaining which forces are essential and which are merely incidental to the operations under observation, and in measuring their magnitude. Then only does it become possible to treat mineral solutions at high temperatures substantially like other chemical solutions at lower temperatures, and to utilize the experience gathered by modern chemistry during the last quarter of a century.

"The method of actual procedure and the progress so far made can also be outlined in a general way quite briefly. We must begin with the simplest problems, and proceed in an orderly way to those more complicated—first, the properties of single minerals over the entire range of their stable existence (solid and liquid); then combinations of two, in which both remain stable; then similar combinations in which exceptional phenomena occur; then simple rocks of three components, etc.—the general principle of effective progress being to meet and study the unknown phenomena *one at a time*. Our studies hitherto have, therefore, been confined to single minerals and to comparatively stable combinations of two under usual atmospheric conditions. The modified conditions which may be produced by an atmosphere of carbon dioxide, or water vapor under pressure, or by pressure alone, have been taken up only in certain special cases, and their systematic development is dependent upon more favorable laboratory conditions * * *."

ARTHUR L. DAY, *Report on Geophysical Research, Year Book No. 5, (1906) of the Carnegie Institution of Washington.*

FOREWORD

In the year 1905 the Carnegie Institution of Washington authorized the construction of a geophysical laboratory for the purpose of continuing and extending the novel experimental work that had been conducted by Dr. Arthur L. Day and his associates in the laboratories of the United States Geological Survey under special grants by the Institution. The building, occupying an advantageous site in the northwest section of the city of Washington, was completed during the latter part of June, 1907, under the supervision of Doctor Day who continued as Director of the Laboratory until his retirement in 1936.

Leading geologists had long been aware of the need for a systematic study of rock formation. By the establishment of the Geophysical Laboratory it became possible to carry out such investigations in a truly comprehensive manner and to examine in detail the properties and behavior of silicate magmas. With rare insight, and with a courage that in our present state of enlightenment can not readily be appreciated, Doctor Day elected to consider a magma merely as a silicate solution, containing a finite number of simple components and amenable to well-known laws. A physicist by training, he brought to this undertaking a keen appreciation of the value of exact measurement, and he set as his goal the establishing of petrology as a quantitative science. As shown by the accompanying quotation, he also outlined in convincing terms the purpose and plan of this ambitious venture. How well these purposes have been achieved may best be judged by the tangible results in the form of published information. The publications of the Laboratory now number one thousand and contain a vast amount of knowledge which is being successfully employed in the interpretation of geological observations and in deciphering Earth's history as recorded in the igneous rocks.

This volume contains a series of papers presenting the results of current research by members of the Laboratory. The articles constitute a cross-section of the program of the Geophysical Laboratory, and cover a wide range of subjects now under investigation. To the foresight, leadership, and wise counsel of Doctor Day, whose work possible, his colleagues respectfully dedicate this volume.

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THE FREEZING-POINT—SOLUBILITY CURVES OF HYDRATES AND OTHER COMPOUNDS UNDER PRESSURE.

LEASON H. ADAMS.

ABSTRACT.

For the determination of equilibrium in systems under high pressure there are two principal modes of attack. We may either devise an experimental method for measuring directly the solubility at the various pressures, or determine indirectly the variation of concentration with pressure under conditions of equilibrium by measuring the compressibilities of the several phases and applying a simple thermodynamic relation. It has already been shown by previous studies at this Laboratory that for simple systems under pressures of several thousand bars (metric atmospheres) the indirect thermodynamic method is convenient and precise. Equilibrium curves for more complex cases, in which hydrates and other compounds appear, are now considered in detail and the various equations used in passing from volume-change measurements to points on the freezing-point—solubility curves are set forth. The method is illustrated by the determination of the solubility curve of a salt hydrate under pressure, and other representative types of equilibrium diagrams are discussed.

INTRODUCTION.

A study of the formation of rocks under the conditions that exist within the Earth resolves itself into detailed investigations of the influence of temperature and pressure on various combinations of minerals. In the Earth both temperature and pressure increase steadily from the surface downward. We recognize temperature as an essential factor in petrology because of well-known thermal effects, and we infer the importance of pressure because at a depth of only 30 kilometers, which is within what is commonly called the crust of the Earth, pressures of nearly 30,000 atmospheres must exist. It is evident that in experimental petrology it is necessary to take account of pressure as well as temperature, and to investigate melting phenomena of minerals and combinations of minerals subjected to pressures of considerable magnitude. Although there has been more progress on the purely

thermal side, a beginning has been made in the study of melting-point and solubility curves for mixtures under high pressure. The recent development of the necessary technique will doubtless lead to much further work in this important field of experimentation. Two classes of methods, direct and indirect, have been used in determining equilibrium in systems under pressure. By the first type of method we measure directly the change of solubility, for example, or some property associated with this change. On the other hand, by the second kind of method we take advantage of a simple and useful thermodynamic principle and measure merely the compressibilities of the various solutions and other phases occurring in the system, and from these measurements of volume-change calculate various points on the freezing-point or solubility curve. For application to systems under pressures of several thousands of atmospheres the indirect, or thermodynamic, method seems more convenient as well as more accurate.¹ The thermodynamic principle utilized in this indirect method is that equilibrium in a physical-chemical system is dependent on the chemical potential of the separate phases and that the chemical potential at various pressures is related very simply to the change of volume under pressure.

THE THERMODYNAMIC METHOD.

Simple Cases.

The principle involved may be summarized by the two equations,

$$\mu'_1 = \mu''_1 \quad (1)$$

$$\frac{d\mu'_{1\bullet}}{dP} = v'_1 \quad (2)$$

According to the first equation the necessary and sufficient condition for equilibrium may be expressed in terms of the chemical potential (μ) of any component. The equilibrium with respect to component (1), for example, in the two phases indicated by the superscripts prime and double prime is determined by the equality of the corresponding μ 's. The meaning of the second equation is that as the pressure varies, the tem-

¹ Adams, L. H.: J. Am. Chem. Soc., 53, 3769-3813, 1931.

perature and composition remaining constant, the change in the μ of component (1) is determined by the product of the pressure-change and the quantity \bar{v}_1 , which is called the fictive volume of the component and is evaluated from measurements of the densities (ρ) of the solutions, or of their reciprocals, the specific volumes (v), by means of the expression

$$\bar{v}_1 = v + x_2 \left(\frac{\partial v}{\partial x_1} \right)_{P, T} \quad (3)$$

In a binary solution at any given constant pressure and temperature this equation is applicable to any value of x_1 , the weight-fraction of the component under consideration (x_2 being the weight-fraction of the other component and therefore equivalent to $1 - x_1$). By the interchange of subscripts, equations (1), (2) and (3) become applicable to the other component of the binary system. It should be noted that the thermodynamic method is not restricted to binary systems but applies equally well to a system containing any number of components.

The experimental methods for measuring the volume-changes required for the determination of the freezing-point or solubility curve have already been described in full detail.^{2, 3} It is sufficient at this time merely to recall that the densities at atmospheric pressure and the compressions of the various solid phases and of solutions at several concentrations are measured with as much precision as possible; the effective specific volumes, in solution, of each component (i.e. the fictive volumes) are then computed by means of equation (3) or a modification of it. Next, by the use of the relation expressed in equation (2), the chemical potential (μ) of each component in solution is calculated for a suitable range of pressures and concentrations, and finally, the pressure at which, for each concentration, the respective μ 's of a given component in the two phases become equal is determined. This establishes a series of points on the equilibrium curve in the system under consideration. We find for example⁴ that μ_2 , the potential of NH_4NO_3 in an aqueous solution containing 29.7 per cent (by weight) becomes equal at 10,000 bars to μ_s , the potential of solid NH_4NO_3 at the same pressure and at the same temperature, namely 25° . Therefore, the solubility of NH_4NO_3 ,

² Ref. 1, pp. 3773-3780.

³ Gibson, R. E.: J. Am. Chem. Soc., 53, 1522, 1937.

⁴ Adams, L. H., and Gibson, R. E.: J. Am. Chem. Soc., 54, 4520-4537, 1932.

4. *Leason H. Adams—Solubility Curves of*

which at atmospheric pressure is 67.6 per cent, is decreased to 29.7 per cent by subjecting the system to a pressure of 10,000 bars.

In order to facilitate the calculation, we deal with the *differences* between the μ 's in the various solutions and the μ 's in some reference state. Accordingly we write equation (1) in the form

$$\mu_s - \mu_l = \mu_1 - \mu_i \quad (4)$$

from which by equation (2) we have

$$\int_{P_i}^P (v_s - v_l) dP = (\mu_1 - \mu_i)_0 + \int_0^P (v_1 - v_l) dP \quad (5A)$$

as the condition of equilibrium in convenient form for calculating the freezing-point curve, under varying pressure, of a component that is liquid at atmospheric pressure. Here P_i refers to the freezing-pressure of the pure component (1), and the subscripts s and l refer respectively to the pure liquid (1) and to the pure solid (1). Zero, when used as a subscript or as one of the limits of integration, refers to atmospheric pressure. The determination of points on the freezing-point curve is carried out by first plotting as ordinates the values of the left-hand member of equation (5A) at various pressures, and then for a number of concentrations (e.g. various x_2 's) plotting a series of curves each expressing the numerical value of the right-hand member of equation (5A) as a function of pressure at the given constant x_2 . It is convenient to use either graphical or tabular integration. The intersections of the first curve with the curves for the various x_2 's obviously give pairs of values of P and x_2 for which there is equilibrium between solid and liquid, and thus yield a series of points on the P - x_2 or freezing-pressure, curve.

This particular method, which involves the plotting of a series of μ - P curves at constant x , will be called Procedure A. An alternative method is based on the following equation, which is obtained by rearrangement of equation (5A),

$$(\mu_1 - \mu_i)_0 = - \int_0^{P_i} (v_1 - v_l) dP - \int_{P_i}^P (v_1 - v_s) dP \quad (5B)$$

Because the left-hand member of this equation is a function of x_2 , we may determine the freezing-pressure of solutions

of various concentrations by first plotting $(\mu_1 - \mu_1)_0$ as ordinate with x_2 as abscissa, and then finding the intersections of this curve with the separate curves obtained by plotting as ordinates

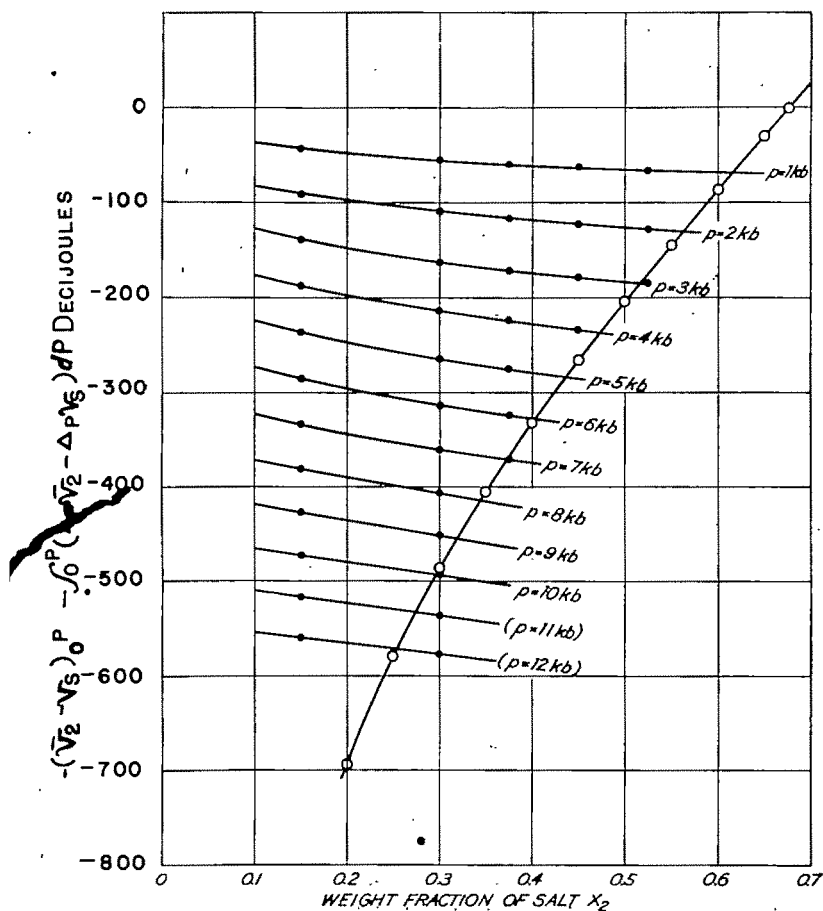


Fig. 1 (after Adams and Gibson). Illustration of method for determining points on a solubility curve by noting the intersections of curves for chemical potential.

the values of the right-hand member of equation (5B) at constant pressure and varying concentration. According to Procedure B, therefore, we determine equilibrium by means of a series of $\mu-x$ curves at constant P .

If the equilibrium curve pertains to a phase that is solid at atmospheric pressure (and at the temperature under consideration), the working equation for use by Procedure A takes the form

$$\int_0^P (v_s - v'_2) dP = (\mu_2 - \mu'_2)_0 + \int_0^P (\bar{v}_2 - v'_2) dP \quad (6A)$$

In this instance we are dealing with component (2), and the superscript prime here refers to concentration at which the

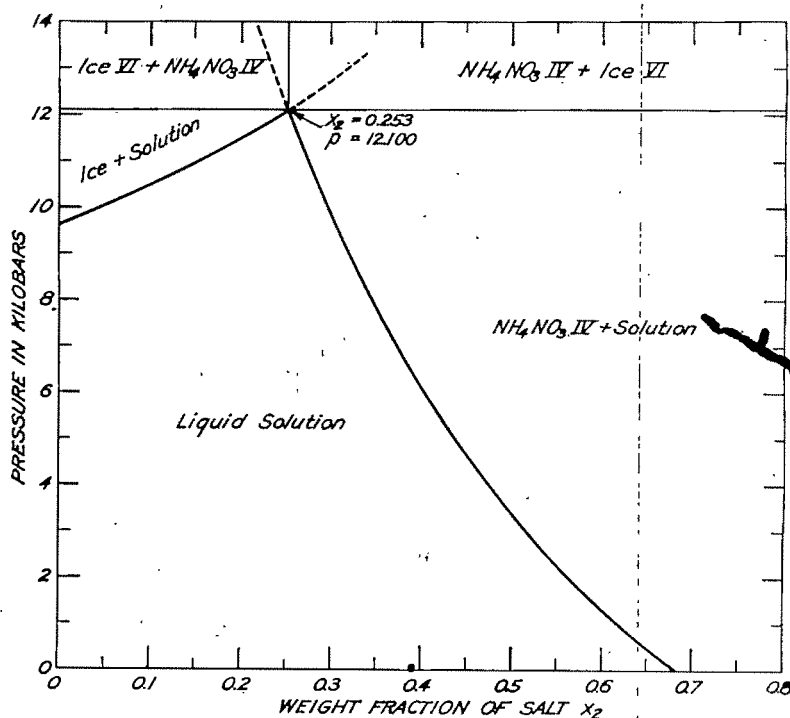


Fig. 2 (after Adams and Gibson). Equilibrium diagram for the system, $\text{NH}_4\text{NO}_3\text{--H}_2\text{O}$, at 25° . The solubility curve shown on the right was determined graphically as shown in Fig. 1.

solution is saturated (at one atmosphere) and in equilibrium with solid component (2). As before, points on the equilibrium curve are determined by plotting the left-hand member of the equation with P as abscissa and finding the intersections of this curve with the family of curves obtained by plotting

the right-hand member of equation (6A) with variable P and constant x_2 . The alternative form of the equation—obtained by a slight rearrangement—is

$$(\mu_2 - \mu'_2)_0 = - \int_0^P (\bar{v}_2 - v_s) dP \quad (6B)$$

Because it is convenient in the course of the computation to deal with the *volume-changes* ($\Delta_p v$) under pressure rather than the volumes at the various pressures, more useful forms of (6A) and (6B) are obtained by putting $v_s = (v_s)_0 + \Delta_p v_s$ and $\bar{v}_2 = (\bar{v}_2)_0 + \Delta_p \bar{v}_2$, and noting that the integral of $(v_s)_0 dP$ is $(v_s)_0 P$, whereupon we have

$$\begin{aligned} (v_s - \bar{v}_2)_0 P + \int_0^P (\Delta_p v_s - \Delta_p \bar{v}_2) dP \\ = (\mu_2 - \mu'_2)_0 + (v_2 - v'_2)_0 P + \int_0^P (\Delta_p \bar{v}_2 - \Delta_p v_s) dP \end{aligned} \quad (7A)$$

and

$$(\mu_2 - \mu'_2)_0 = -(\bar{v}_2 - v_s)_0 P - \int_0^P (\Delta_p \bar{v}_2 - \Delta_p v_s) dP \quad (7B)$$

Probably the most generally useful in actual practice are equation (5A) for determining the freezing-point curve of an originally liquid component, and equation (7B) for the solubility curve of an originally solid component. An example of the application of the latter equation is shown in Figs. 1 and 2, which are taken from the paper by Adams and Gibson⁴ on the system, $\text{NH}_4\text{NO}_3\text{--H}_2\text{O}$. The intersections of the curve for $\mu_2 - \mu'_2$, in Fig. 1, with the family of curves representing the right-hand member of equation (7B) (as well as 6B) yield the points on the part of the diagram in Fig. 2 that pertain to the solubility of NH_4NO_3 under pressure.

Hydrates and other Compounds.

Having summarized the necessary steps in determining equilibrium curves by the thermodynamic method for simple cases, we proceed now to consider equilibrium curves involving hydrates and other compounds. Compared with the procedure for the simple cases discussed above, the principal difference is due to necessity for choosing new components and for interrelating their properties. It is well known that the thermodynamic treatment of physical-chemical systems is facilitated by a proper choice of components and that it is allowable to

choose as the components in a system any compounds or mixtures in terms of which the compositions of the several phases may be expressed. For some purposes it is necessary to include among the chosen components a composition equivalent to that of any solid phase under consideration, if that phase is invariant in composition. For example, in dealing with the system, $\text{NaCl}-\text{H}_2\text{O}$, under circumstances in which the hydrate, $\text{NaCl}\cdot 2\text{H}_2\text{O}$, makes its appearance, we must select $\text{NaCl}\cdot 2\text{H}_2\text{O}$ as one component of the aqueous solution, the other component then being any convenient quantity such as for example excess or deficiency of water.

It is important to note the transformation equations for the various components that may be selected. From elementary principles it follows that

$$\bar{v}_3 = (1 - x_o) \bar{v}_1 + x_o \bar{v}_2 \quad (8)$$

$$(\mu_3 - \mu'_3) = (1 - x_o)(\mu_1 - \mu'_1) + x_o(\mu_2 - \mu'_2) \quad (9)$$

in which the subscript, 3, refers to the component whose composition is that of the hydrate or other compound, and x_o denotes the weight-fraction of anhydrous salt in the hydrate itself. Subscripts 1 and 2, as before, refer respectively to pure solvent and anhydrous salt. Because in many instances the properties of the solutions expressed in terms of components 1 and 2 are already available, it usually is unnecessary to compute \bar{v}_3 and μ_3 directly from the original measurements.

By analogy with equation (6A) or (6B) we have

$$\int_0^P (v_o - \bar{v}'_3) dP = (\mu_3 - \mu'_3)_o + \int_0^P (\bar{v}_3 - \bar{v}'_3) dP \quad (10A)$$

or

$$(\mu_3 - \mu'_3)_o = - \int_0^P (\bar{v}_3 - v_o) dP \quad (10B)$$

in which v_o denotes the specific volume of the solid compound. From (8) and (9) it follows that

$$\int_0^P (v_o/x_o - \bar{v}'_2 - \bar{v}'_1/r_o) dP = (\mu_2 - \mu'_2)_o + (\mu_1 - \mu'_1)_o/r_o + \int_0^P [(v_2 - v'_2) + (v_1 - v'_1)/r_o] dP \quad (11A)$$

$$(\mu_2 - \mu'_2)_o + (\mu_1 - \mu'_1)_o/r_o = - \int_0^P (v_2 + v_1/r_o - v_o/x_o) dP \quad (11B)$$

r_0 being the equivalent of $x_0/(1-x_0)$. These equations are in form for calculating the solubility curves for hydrates by Procedures A and B described above and are directly applicable to hydrates stable at atmospheric pressure. Probably (11B) is the more generally useful form.

In actual practice it will usually be preferable to make the same change in equations (11A) and (11B) as was made in

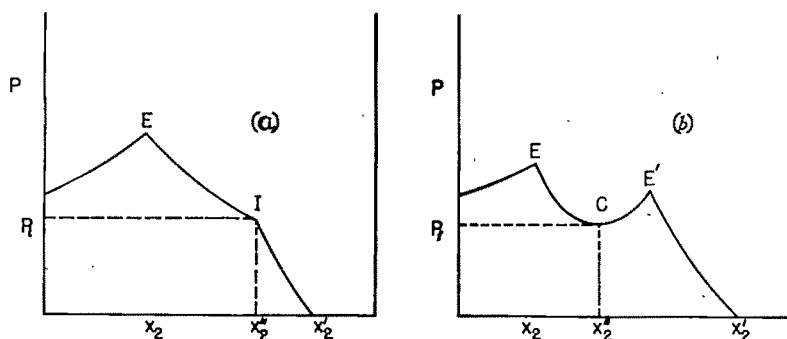


Fig. 3. Schematic diagram showing equilibrium curves under pressure on system involving a hydrate or other compound that (a) melts incongruently and (b) melts congruently.

transforming equations (6A) and (6B) to (7A) and (7B), namely to replace \bar{v}_1 by $(\bar{v}_1)_0 + \Delta_p \bar{v}_1$, and similarly for \bar{v}_2 and \bar{v}_o .

If at a temperature that is higher than the temperature T for which the $P-x$ diagram is being constructed a salt hydrate melts incongruently to a mixture of anhydrous salt and solution, and if the transformation temperature is lowered by pressure so that at the temperature T and at or above a pressure P_i the anhydrous salt rather than the hydrate becomes the phase that is stable in contact with solution, then the equilibrium diagram may take a form similar to that shown in Fig. 3a. The complete solubility curve for the salt consists of two branches, one pertaining to the hydrate and the other to the anhydrous salt. The first of these, which is readily evaluated by equation (11), begins at atmospheric pressure (substantially zero on the scale of this diagram) and extends to the transformation point I where it intersects the solubility curve of the anhydrous salt. Evaluation of the latter curve is carried by means of the expression obtained by suitable change of the

limits of integration in equations (6) or (7). We thus obtain, for example,

$$\int_{P_i}^P (v_2 - v''_2) dP = (\mu_2 - \mu''_2)_0 + \int_0^P (v_2 - v''_2) dP \quad (12A)$$

$$(\mu_2 - \mu''_2)_0 = - \int_0^{P_i} (v_2 - v''_2) dP - \int_{P_i}^P (v_2 - v_2) dP \quad (12B)$$

For this purpose we may also use equation (6B) or (7B) without alteration other than changing μ'_2 to μ'''_2 , the μ of the solution (metastably) saturated with respect to the anhydrous salt (at $P=0$), thus beginning our calculation at atmospheric pressure and with the initial, metastable, portion of the solubility curve.

If on the other hand the incongruent melting-temperature is initially lower than T and is raised by pressure, then at a pressure P_i the hydrate enters the $P-x$ diagram. For this case the low-pressure branch of the solubility curve pertains to anhydrous salt, and the high-pressure branch, extending from I to E in Fig. 3a, pertains to the hydrate. The first branch may of course be determined by equation (6) or (7). For the hydrate curve a slight modification of (11) is required in order to take into account the changed limits of integration. Convenient forms of equations for a hydrate curve beginning at pressure P_i and concentration x''_2 are

$$\int_{P_i}^P (v_2/x_0 - v''_2 - v''_1/r_0) dP = (\mu_2 - \mu''_2)_0 + (\mu_1 - \mu''_1)_0/r_0 + \int_0^P [\bar{v}_2 - v''_2 + (\bar{v}_1 - v''_1)/r_0] dP \quad (13A)$$

$$(\mu_2 - \mu''_2)_0 + (\mu_1 - \mu''_1)_0/r_0 = - \int_0^{P_i} [\bar{v}_2 - v''_2 + (\bar{v}_1 - v''_1)/r_0] dP - \int_{P_i}^P (\bar{v}_2 + \bar{v}_1/r_0 - v_2/x_0) dP \quad (13B)$$

Just as with previous equations, it is often preferable to deal with volume-changes rather than with volumes. We therefore may substitute, in equations (13A) or (13B), $(\bar{v}_1)_0 + \Delta_p \bar{v}_1$, for example, in place of \bar{v}_1 , in order to obtain the final working equation.

In the event that the hydrate under consideration melts con-

gruently the equilibrium diagram may resemble that shown in Fig. 3b. The curve for hydrate-solution equilibrium has a minimum at C , the point at which the concentration x_2 of (anhydrous) salt in the solution equals x_0 , the weight-fraction of anhydrous salt in the solid hydrate. At E and E' the hydrate curve intersects equilibrium curves of other solids. These intersections thus mark the compositions and freezing-pressures of eutectics analogous to those encountered in $T-x$ diagrams. It is easily shown that an appropriate and convenient equation for determining the equilibrium curve of a compound that melts congruently is obtained from equation (13B) by merely replacing P_i in that equation by P_f , the freezing-pressure (at temperature T) of the pure compound, and noting that x''_2 is now equal to x_0 . A separate measurement of P_f is obviously required.

It is important to note that the shape of the equilibrium curve is a consequence of the theorem enunciated by Gibbs⁵ to the effect that when a compound has been chosen as one of the components in a system, the other component being a part of this compound, then μ_3 , the chemical potential of the compound, has its greatest value when the solution has the composition of the compound. That is, μ_3 (or $\mu_3 - \mu''_3$, or $\mu_2 - \mu''_2 + (\mu_1 - \mu''_1)/r_0$), when plotted as a function of x_2 , will have a maximum at $x_2 = x_0$. Therefore, a curve representing the right-hand member of (13B) may, for certain values of P , intersect the curve of $\mu_3 - \mu''_3$ at two points and thus yield two points on the desired solubility, or freezing-point, curve. A further consequence is that $P-x$ as well as $T-x$ curves must have a maximum or minimum at the composition of the compound.

A more general case of two hydrates may also be represented diagrammatically by Fig. 3a, if we suppose the low-pressure branch of the solubility curve to refer to one hydrate and the high-pressure branch to a second hydrate, P_i being the pressure at which the incongruent melting or freezing takes place. In this instance, also, equation (13B) gives us the condition of equilibrium along the curve for either hydrate. Under these circumstances x_0 is the weight-fraction of anhydrous salt in the particular hydrate under consideration, v_0 is its specific volume, and x''_2 is the composition of the solution at the low-pressure end of the equilibrium curve for the compound.

⁵ Gibbs, J. W.: Scientific Papers, New York, Vol. I, pp. 93, 99, 135, 1906.

Indeed, equation (13B) is a general one from which the equations pertaining to all the types of curves previously discussed may be obtained. For example, by putting $P_i = 0$, $x_o = 1$, $v_o = v_s$, and $x''_2 = x'_2$, we obtain equation (6B) for a simple solubility curve beginning at atmospheric pressure. The appropriate equation (12B), for an anhydrous salt stable only at high pressures, may be obtained from (13B) by putting $x_o = 1$ and $v_o = v_s$. It should be noted that equation (12B) applies also to a solid that inverts at P_i from one form to another without change of composition. To obtain the equation (11B), for a hydrate curve beginning at atmospheric pressure we put $P_i = 0$ and $x''_2 = x'_2$. Finally, the equation (5B), for determining the freezing-pressure curve of the solvent, may be derived from (13B) by substituting P_f for P_i , and putting $v_o = v_s$, $x_o = 1$, and x''_2 (which now becomes x''_1) = 1, that is, $\bar{v}_2 = \bar{v}_1$ and $\mu''_2 = \mu_1$.

EXAMPLE OF EQUILIBRIUM CURVE FOR A HYDRATE UNDER PRESSURE.

A portion of the $P-x$ diagram for the system, $\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$, at 25° will serve as an illustration of the determination of a hydrate equilibrium curve by the thermodynamic method. At 25° the stable solid phase in contact with solution is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and the saturated solution contains 21.8 per cent by weight of Na_2SO_4 . Anhydrous Na_2SO_4 at atmospheric pressure becomes stable only above the incongruent melting-point, 31.38 per cent. Some unpublished measurements by Dr. R. E. Gibson and the author on the compression of Na_2SO_4 solutions readily yield values of \bar{v}_1 and \bar{v}_2 at various pressures and concentrations. The chemical potentials, μ_1 and μ_2 , of H_2O and Na_2SO_4 in the solutions at atmospheric pressure may be derived from published data on the vapor pressure and freezing-points of Na_2SO_4 solutions and on the emf.'s of cells involving Na_2SO_4 . Although the compression of anhydrous Na_2SO_4 has been measured,⁶ that of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ has not yet been determined. Even though this datum is lacking, it is possible to construct an equilibrium diagram of moderate accuracy, because it happens that at low pressures the compression of the decahydrate is not an important factor in the calculation and that the decahydrate at 25° is stable only at moderate pressures. Based upon our knowledge of the compressions of

⁶ Adams, L. H., and Gibson, R. E.: J. Wash. Acad. Sci., 21, 381-390, 1931.

various solids the assumption will be made that the compression of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is 4×10^{-6} reciprocal bars. It is not likely that the true compression differs sufficiently from this amount to introduce a serious error into our computations.

The necessary data being on hand, equation (11B) was used to determine the solubility curve of the decahydrate at 25° . In Fig. 4 is shown a plot of $(\mu_2 - \mu'_2) + (\mu_1 - \mu'_1)/r_0$, the

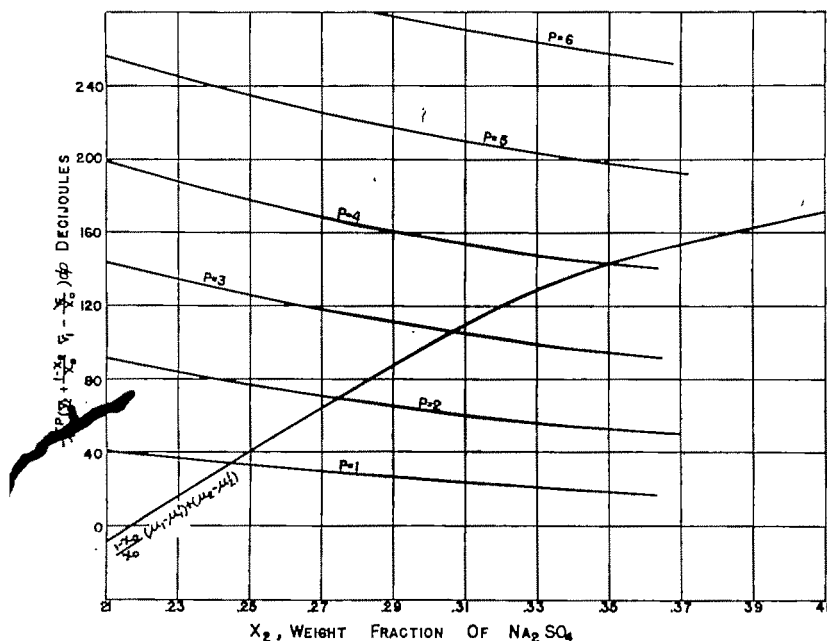


Fig. 4. Chemical potential curves for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ under pressure, used for the graphical solution of equation (11B).

left-hand member of (11B), as a function of x_2 . As before, r_0 is the equivalent of $x_0/(1 - x_0)$. In the same figure the right-hand member of (11B) for a series of constant pressures, viz. 1, 2, 3, 4, 5 and 6 kilobars respectively, is also plotted as a function of x_2 . As explained above, the intersections shown in this diagram yield points on the solubility curve of the decahydrate. At 1000, 2000, 3000 and 4000 bars the values of x_2 are found by this procedure to be 0.246, 0.275, 0.307 and 0.350 respectively. From the circumstance that the curve for $\mu_2 - \mu'_2 + (\mu_1 - \mu'_1)/r_0$ is concave downward (having a maximum at $x = 0.441$) and that the other curves in Fig. 4

are concave upward, it becomes probable that the curve for $P=5$ kilobars does not intersect the μ -curve and that the decahydrate, therefore, is not stable at pressures as high as 5000 bars (at 25°). This supposition is confirmed by Fig. 5 in which there are plotted the points obtained for the solubility curve of the decahydrate as well as a curve for the solubility of the anhydrous salt under pressure. This curve was obtained

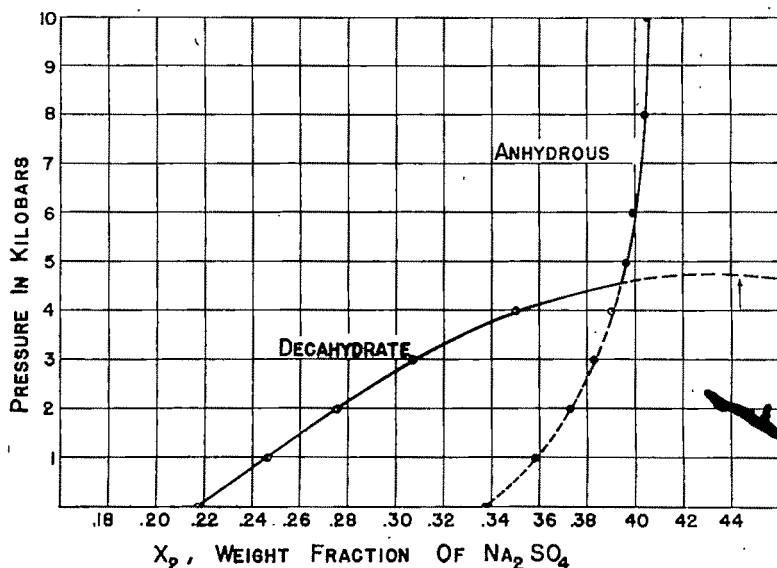


Fig. 5. A portion of the equilibrium diagram for the system, $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$, at 25° . The solubility of the decahydrate was obtained from the intersections of the curves drawn in Fig. 4.

by the application of equation (7B) to the data mentioned above. It begins at low pressure as a metastable portion of the solubility curve and appears to have a flat maximum of x_2 at about 10,000 bars. The intersection with the hydrate curve determines the transition-pressure, which is thus found to be 4600 bars at 25° —in substantial agreement with unpublished direct measurements (by Dr. Gibson and the author) of the pressure at which incongruent melting takes place.

By inspection of Fig. 5 it will be seen that the solubility curve of the hydrate, like the curve for μ , is concave towards the x_2 -axis, which is in accord with the circumstance that the curve must have a horizontal tangent at the point corresponding

to x_0 , that is, at the point, $x_2 = 0.441$, indicated by the arrow. The significant fact is that whereas for anhydrous salts dx_2/dP , the rate of increase of solubility with pressure, even when positive, becomes less at the high pressures, the solubility of the hydrate, on the contrary, may increase at a rate that becomes greater as the pressure increases. The result is that in the present instance the two curves for decahydrate and anhydrous salt, respectively, intersect at a relatively low pressure, thus causing the hydrate to be stable only within a limited pressure range.

REPRESENTATIVE TYPES OF FREEZING-POINT DIAGRAMS.

A consideration of the factors involved in the various equations previously set forth for calculating equilibrium relations under pressure by the thermodynamic method gives us important information concerning the various possible types of freezing-point curves in binary systems. Some conclusions as to the merely qualitative aspects of various types of diagrams are illustrated in Fig. 6. The shaded portions of the various fields represent the conditions under which the mixtures are entirely liquid. The first group (a) pertains to simple systems that do not involve compounds. Nos. 1 to 6 of this group show in succession diagrams for two components both of which are solid at atmospheric pressure; for one component solid and the other liquid at atmospheric pressure; for both components liquid; for a component whose solubility at first increases and then decreases under pressure; for one component having an enantiotropic inversion; and for both components having such inversions.

The diagram (b1) illustrates the case of a hydrate the incongruent melting-temperature of which is lowered by pressure so that at constant temperature there is an incongruent melting at a certain pressure. The solubility curve on the right-hand side of the diagram at the lower pressures pertains to hydrate and at the higher pressures to the anhydrous salt or another hydrate. Diagram (b2) shows the appearance of a $P-x$ diagram for the same system but at a higher constant temperature, namely one that is above the incongruent melting-temperature. The solubility curve on the right is for the anhydrous salt, and under the conditions specified the hydrate does not come into the diagram. In diagram (b3) we have the same conditions as in (b1) except that the solubility of the

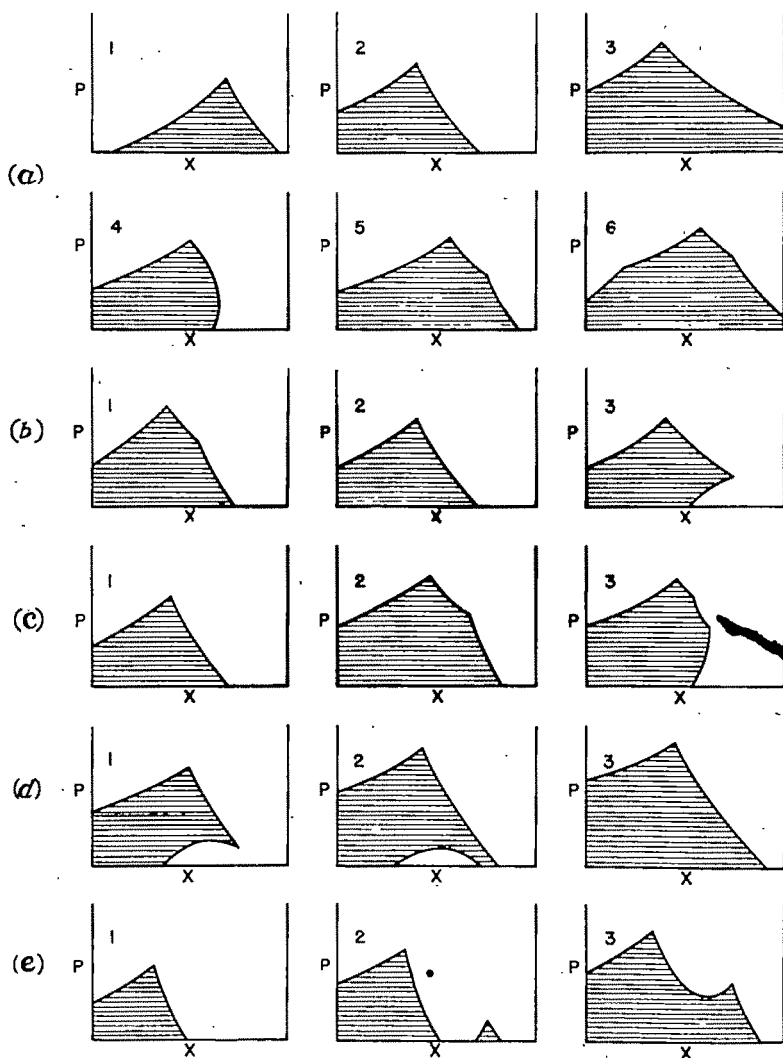


Fig. 6. Representative types of equilibrium diagrams for binary systems under pressure.

hydrate is increased rather than decreased by pressure. In this respect the diagram resembles the one for the system, $\text{Na}_2\text{SO}_4\text{—H}_2\text{O}$.

For systems in which there is encountered an incongruent

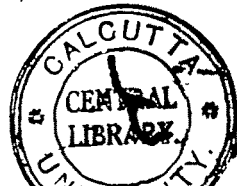
melting-point that is raised by pressure we may have diagrams similar to those in group (c). The first of these, (c1), pertains to a temperature below the transformation temperature, and is similar to (b2) except that here the right-hand equilibrium curve is that of the hydrate rather than that of the anhydrous salt. If the constant temperature under consideration is above the transformation, equilibrium curves as in (c2) will usually be obtained. The case of an incongruent melting-temperature that is first raised by pressure and then lowered (the melting-point thus showing a maximum) is illustrated by (c3). This diagram closely resembles the one for the system,⁷ NaCl—H₂O, at 25°, which is below the maximum temperature on the $P - T$ curve for the hydrate. In this case increasing pressure causes the hydrate to appear and then to disappear at a somewhat higher pressure.

If the hydrate, or other compound, melts congruently and if the melting-temperature is depressed by pressure, the series of diagrams (d) are obtained. The first is at a temperature below the melting-temperature of the compound and below also the eutectic (on the $T - x$ diagram) between the compound under consideration and the adjacent solid. Diagrams (d2) and (d3) refer, respectively, to temperatures that are above the eutectic-temperature but below the melting-temperature, and to temperatures above both the melting-temperature and the eutectic-temperature. It is of course unusual for the melting-temperature of a substance to be lowered by pressure, but it is not unlikely that among hydrates some examples of this will be found. It is worthy of note that the general relations shown in (d1) or (d2) are approached though not attained in the sodium sulphate system.

For the more usual case of a compound the melting-temperature of which is raised by pressure we have the diagrams (e1), (e2) and (e3). In the first the temperature is below both the melting-temperature of the compound and an adjacent eutectic-temperature; in the second the temperature is still below the melting-temperature but is above the eutectic-temperature, and in the third the temperature is above both transformation-temperatures.

The equilibrium curves shown in Fig. 6 do not cover all the possible types of equilibrium diagrams for systems under pressure, but they represent the ones that will most commonly be

⁷ Adams, L. H., and Gibson, R. E.: J. Am. Chem. Soc., 52, 4252-4264, 1930.




encountered and they serve to illustrate the correspondence between $T - x$ and $P - x$ diagrams.

CONCLUDING REMARKS.

In the foregoing discussion of equilibrium diagrams nothing has been said concerning solid solutions. Melting-point curves for systems in which this effect occurs may be determined by the same methods as have been described for systems involving solids of constant composition. By a slight extension of the equations that have been presented they become applicable to equilibria between solid solutions and other phases, as well as to systems containing any number of constituents.

It is interesting to compare the methods used in high-pressure and in high-temperature investigations of systems containing two or more components. Indirect methods may be employed in either field of research, but for the determination of equilibrium relations at high pressures the indirect thermodynamic method has peculiar advantages. This is because equilibrium under pressure depends upon volume, which can be measured with unusual precision. On the other hand, direct observation of phenomena taking place within a container sufficiently strong to withstand a pressure of several thousand atmospheres involves great experimental difficulties, which hinder the attainment of satisfactory accuracy. The indirect method will doubtless find increasing use in studies of the melting behavior of mixtures under high pressures, and when applied to silicate solutions will serve as an important tool in the solving of petrologic problems.



LAVAS OF THE AFRICAN RIFT VALLEYS AND THEIR TECTONIC SETTING.

NORMAN L. BOWEN.


ABSTRACT.

The state of knowledge and opinion as to the African Rift Valleys and their lavas was, a decade ago, such as to suggest that a definite correlation might be made between the tectonics and the chemistry of the lavas. The Western Rift Valley seemed to have been formed as a result of compressive stresses in the crust and to have associated with it lavas of potash-rich character. The Eastern Rift Valley seemed to have been formed as a result of tensional stresses and to have associated with it lavas of soda-rich character. The picture now presented is less simple. As a result of further investigation there has arisen much diversity of opinion as to the tectonic forces controlling the formation of both Rift Valleys, and there seems therefore no adequate basis for an attempt to correlate lava chemistry with contrasted tectonics. In addition, recent studies of the lavas have brought to light many exceptions to the general tendency towards preponderance of potash in the Western Rift and preponderance of soda in the Eastern Rift. Some new analyses are given which illustrate these exceptions and emphasize the fact that, as in the case of the tectonic relations, no simple picture of the chemistry of the lavas can be outlined at the present time. Indeed, when the question of the origin of the dominant lavas of the Western Rift is reviewed in the light of latest knowledge, their potash-rich character seems to be a relatively accidental circumstance. This question is discussed and the lack of any convincing relation between lava chemistry and tectony in the Rift Valleys is emphasized.

INTRODUCTION.

In 1929 the opportunity came of making a field study of the volcanic rocks of the African Rift Valleys under the auspices of the Carnegie Institution of Washington, a welcome opportunity, especially since the investigation was to be made in conjunction with structural investigations of these earth features by Professor Bailey Willis. At that time the picture of Rift Valley relations to be gained from the literature was somewhat as follows. (See Fig. I.)

In East Africa a structural trough or graben constituting, towards its southern end, the basin of Lake Nyasa, extending with more or less important interruptions and complications in a meridional direction to the basin of Lake Rudolf, turning northeastward through Abyssinia to the Gulf of Aden and



having associated with it volcanic rocks uniformly of a *soda-rich* character.

In Central Africa a similar trough branching from the former near the head of Lake Nyasa, extending, again with

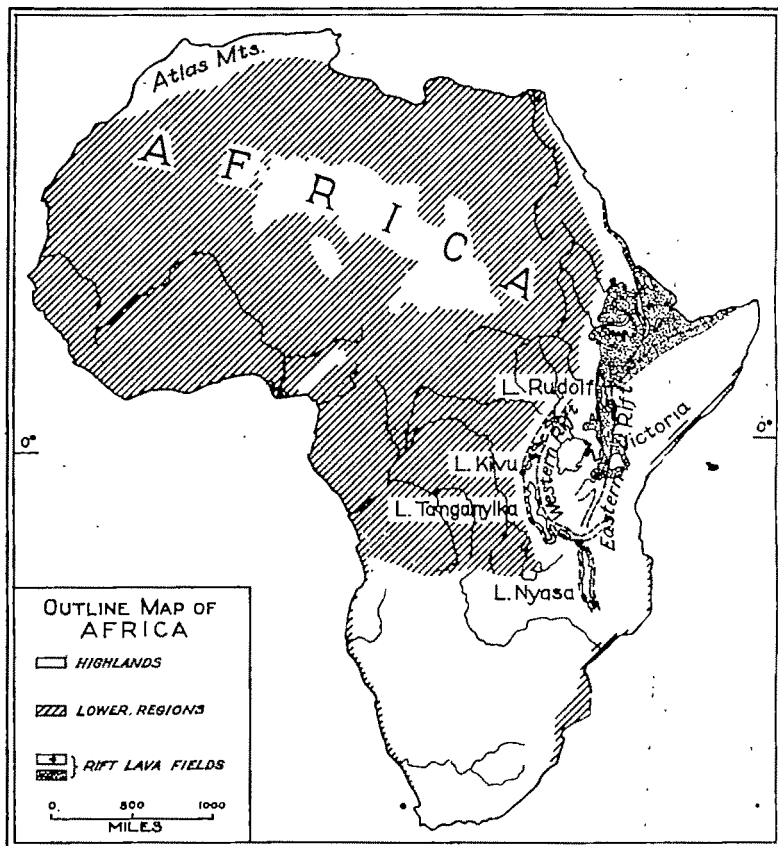


Fig. 1. Map of Africa showing position of Rift Valleys.

certain complications, through the basins of Lake Tanganyika, Lake Kivu, Lake Edward and Lake Albert and having associated with it, though only locally, from Lake Kivu northward, volcanic rocks uniformly of a *potash-rich* character.

With scarcely a dissenting voice, opinion was that the Eastern Rift formed as a result of normal or tensional faulting.

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On the other hand there appeared to be growing support for the opinion advanced by Wayland that the Western Rift, in the vicinity of Lake Albert at least, was formed as a result of overthrust or compressional faulting.

Could it be that here in Africa was offered an unequivocal demonstration of the control of tectonic forces and consequent crustal movements over the chemistry of igneous magmas?

The hypothesis that the tectonic conditions of a region exert some sort of control over the chemistry of the eruptive rocks of the region received its first impetus when Harker, in 1896, pointed out "the very general correspondence of the areas of the alkali and sub-alkali groups respectively with the areas of the Atlantic and Pacific types of coast-line as defined by Suess."¹ This led to the discrimination of an Atlantic suite of igneous rocks corresponding with those that are chemically characterized as the alkalic rocks and a Pacific suite corresponding with the sub-alkalic rocks. The merits of the concept have been much discussed, with the result that it has met with no more than partial acceptance, and in particular the wisdom of the use of terms having geographic connotations has been questioned. Yet this fact has not deterred others from introducing additional terms of like character to designate further distinctions, and thus have arisen the Arctic suite and the Mediterranean suite. The geographic-tectonic implications of the terms are now not usually stressed by those who use them. Pacific suite or branch ordinarily designates, simply, sub-alkalic rocks; Atlantic branch, alkalic rocks in which soda is the dominant alkali; and Mediterranean branch, alkalic rocks in which potash is the dominant alkali. There still adheres, albeit rather loosely, the concept that the Pacific suite is associated with folded mountains and the Atlantic suite with centripetal movement of the crust or crustal foundering. The supposed tectonic affinities of the Mediterranean suite have not been made entirely clear, but the sponsors appear to connect this suite with the early stages of folded chains in substantially the same tectonic setting as the Pacific types.² If, then, the lavas of the Eastern Rift were really uniformly soda-rich and the crustal movement there of a centripetal type, and if, on the other hand, the lavas of the Western Rift were uniformly potash-rich and the crustal movement there of the nature of a thrust, there would appear to be strong support for that kind of relation between tectony

¹ Harker, Alfred: *The Natural History of the Igneous Rocks*, p. 93, 1909.

² Niggli, P.: *Schweiz. Mineralog. petrog. Mitt.*, 2, p. 259, 1923.

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and chemistry that is involved in the concept of Atlantic and Mediterranean suites. What causal connection there could be between tectony and chemistry is a question that could be attacked when and if it was verified that the conditions were really as suggested. There may, too, seem to be serious difficulty in visualizing a condition in which there could be tension on the eastern side and compression on the western side of the block enclosed between the Eastern and Western Rifts, but this difficulty is not insurmountable. We might, for example, imagine a continent which tended to drift westward but had some of its segments more firmly anchored than others. A certain segment with a more marked tendency to drag its anchor might tend to press against its neighboring segment to the west and pull away from its neighbor to the east.³ Probably other conditions, not involving migrating continental blocks, might be imagined to explain this contrast of conditions on opposite sides of a block, were the observed facts definitely such as to encourage such speculation. Unfortunately it has proved, partly as a result of our investigation and partly as a result of later work, that the tectonic contrast suggested is not verifiable and the chemical contrast, while undeniably present in a broad sense, is nevertheless not without exceptions, and the whole picture is therefore not as clear-cut as is desirable for a test case. In the following it is proposed to set forth those findings, and opinions arising from them, that have tended to blur the simple picture.

TECTONICS.

The various opinions that have been held as to the causes of Rift Valleys and the nature of the forces involved in their formation have been summarized in a masterly manner, with apt quotations from the original sources, by Willis in his monographic treatment of these structures in Africa.⁴ The early views of Suess, Gregory and others that the faults were of tensional origin had been questioned in some measure by Uhlig⁵ but no important evidence to the contrary was advanced until Wayland⁶ described what he regarded as reverse faults

³ On this suggestion see Daly: *Geology of Ascension Island*, Proc. Am. Acad. Arts Sci., 60, 19, 1925, and *Our Mobile Earth*, pp. 275-291, New York, 1926.

⁴ Willis, Bailey: *Carnegie Inst. of Wash. Pub. No. 470*, 1936.

⁵ Uhlig, Carl: *Geogr. Z. Leipzig*, 13, 500, 1907.

⁶ Wayland, E. J.: *Geogr. J.*, 58, 244 et seq., 1921.

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in the Albertine Rift. If there had been no further development of diverse views it would have been possible to entertain a picture involving tensional faulting in the Eastern Rift and compressional faulting in the Western Rift. But Willis's own conclusion, which he regarded as applicable to all the rifts, was stated as follows, "It is clear that the causes of the vertical uplift of the plateaus and the associated effects of downward drag are the cause of the rift valleys. Horizontal forces play a subordinate part and as compressive stresses only. Horizontal tension has not been recognized."⁷ To be sure, the only very cogent evidence of horizontal compressive stresses that one finds outlined is the single example of reverse faulting in the Albertine Rift, and Willis himself, setting down the first record of his opinions gained in Africa, expressed agreement with Gregory that the East African Rift (Great Rift Valley) was formed as a result of "stretching."⁸

On the other hand, since Willis's examination observations have been made, especially on the Eastern Rift, that have been regarded as indicating thrust forces. Bullard⁹ has made gravity measurements in the Rift Valleys and on the adjacent plateaus. He finds the plateau as a whole compensated, but the Rift Valleys showing negative anomalies. He concludes therefore that the floor of the Rift Valley would rise were it not pressed down by the adjacent plateau, which has been thrust over it. There are in addition observations by Fuchs¹⁰ on the Lake Rudolf portion of the Rift Valley of which he says "... early Miocene lavas and tuffs are folded by pressure in an east-west direction. Thus, taking the lake as a central line, we found that the folds on either side were overfolded towards it."

Whether Bullard has taken adequate count of the possible presence of very light masses of rock close to the instrument—for there are very light lavas in the valleys and therefore possibly light intrusives not far beneath them—and whether Fuchs' observations will stand, I leave for others and the future to decide. The findings and opinions listed are given merely to emphasize the complete lack of agreement upon a picture of the Rift Valleys such as that suggested on an earlier page, a tensional Eastern Rift and a compressional Western Rift, or

⁷ Willis, Bailey: *op. cit.*, p. 71.

⁸ Willis, Bailey: *Living Africa*, p. 304, New York, 1930.

⁹ Bullard, E. C.: *Phil. Trans. Roy. Soc. London*, A 235, 445-531, 1936.

¹⁰ Fuchs, V. E.: *Geogr. J. London*, 86, 132-133, 1935.

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indeed upon any picture. There is, to be sure, a growing tendency to regard the rifts as the result of compression, yet I should be remiss in recording the facts if I omitted to state that, upon his return from a visit to the Albertine Rift, the late Dr. John W. Evans informed me that he was not convinced that this crucial area for the launching of the compression hypothesis really exhibited reverse or compression faulting.

With such lack of agreement upon tectonic relations there is naturally little encouragement to the petrologist to attempt to correlate tectony and lava chemistry.

COMPOSITION OF THE LAVAS.

Alongside this picture of the unsatisfactory state of knowledge and opinion upon the Rift structures we may place the fact that the chemical composition of the lavas is now known to show less systematic variation than had formerly been supposed to exist. The lavas of the Eastern Rift are nearly all soda-rich but a few examples were collected that show excess of potash over soda and one or two others of this character have since been recorded in the literature. The lavas of the Western Rift are dominantly potash-rich but locally there are areas showing lavas with a distinct excess of soda over potash. It is intended now to give some details regarding these exceptions to the general trend, in other words, some details of the potash-rich lavas of the Eastern Rift and of the soda-rich lavas of the Western Rift.

The lavas of the Eastern Rift normally contain such a marked excess of Na_2O over K_2O that any representative which contains even a small excess of K_2O over Na_2O is worthy of at least passing mention in this connection. The more salic lavas of the Rungwe volcanics, occurring at the head of Lake Nyasa, sometimes contain a slight excess of K_2O over Na_2O . Thus there is a nepheline trachyte with Na_2O 6.04 per cent and K_2O 6.39 per cent and a quartz bostonite with Na_2O 5.68 per cent and K_2O 5.74 per cent.¹¹ In the middle reaches of the Eastern Rift the chemistry of the lavas is best known, but from this section and the neighboring great volcanoes, Kilimanjaro and Mt. Kenya, only one example with even a moderate excess of K_2O has been recorded. This is a rhyolitic obsidian from Lake Naivasha with Na_2O 4.55 per cent and K_2O 4.69 per cent.¹²

¹¹ Lehmann, E.: *Z. Vulkanologie*, 4, 101 and 113, 1924.

¹² Bowen, N. L.: *This Journal*, 33, 14-15, 1937.

Farther to the north, examples become more common both in the Rift and in the neighboring great volcano, Mt. Elgon. In the lavas of Elgon there is a general tendency towards more even balance of the two alkalis and in one leucocratic type, a phonolite, there is Na_2O 6.48 per cent and K_2O 6.52 per cent.¹³ A somewhat more marked development of this relation is shown in a phonolitic trachyte pitchstone collected by Professor Willis at Lake Baringo. The analysis is given in Table I.

TABLE I.
Analyses of Potash-Rich Lavas of the Eastern Rift Valley.

	I	II		I(a)	II(a)
SiO_2	55.65	69.78	Q	...	37.1
Al_2O_3	15.97	6.68	or	37.8	30.0
Fe_2O_3	3.80	5.63	ab	34.1	6.3
FeO	2.77	2.68	ne	6.8	...
MgO	.86	.04			
CaO	1.71	.68	ac	3.2	12.5
Na_2O	5.96	2.42	di	5.3	3.2
K_2O	6.37	5.07	hy	...	1.9
$\text{H}_2\text{O}+$	3.93	5.43	ol	1.2	...
$\text{H}_2\text{O}-$	1.45	1.09	mt	3.9	1.9
TiO_2	.75	.56	il	1.4	1.1
P_2O_5	.16	...	ap	.3	...
Cl	.11	...	CaF_2	.2	...
F	.15	...	hl	.2	...
MnO	.29	.19			
S	.04	...			
	100.06	100.25			
	— .09				
	99.97				

- I Phonolitic trachyte pitchstone, Lake Baringo. R. B. Ellestad, analyst.
 II Pantellerite pitchstone, Turkana. F. Raoult, analyst. E. Jérémme,
 Compt. rend., 198, p. 675.
 I(a) Norm of I.
 II(a) Norm of II.

A very marked excess of K_2O is found in a pitchstone from Turkana, a name given to the country immediately to the west of Lake Rudolf. The analysis by Raoult¹⁴ is here given in Table I. A volcanic plug in the same region has been described

¹³ Ödman, O.: Geol. Fören. Förh., 52, 504, 1930.

¹⁴ In Elizabeth Jérémme, Compt. rend., 198, 673-675, 1934.

as consisting of "pure orthoclase"¹⁵ but Campbell Smith (personal communication) does not accept this observation.

It is probable that for the more extreme cases of richness in potash feldspar a secondary origin is to be inferred, say in the potash-rich pitchstone. Terzaghi¹⁶ suggested that lavas may be enriched in K_2O by hydrothermal after-action and Fenner has shown that this result has come from such action in Yellowstone lavas.¹⁷ Even apart from these extreme cases it is still true that the soda-rich rocks of the Eastern Rift have associated with them types with an excess of K_2O . If tectonic forces controlled the composition of the rocks they did not produce rocks uniformly soda-rich.

The Western Rift does not display vulcanism through such a great proportion of its length as does the Eastern Rift. Towards the south there are no associated lavas; even the spectacular trough occupied by Lake Tanganyika, with its bottom locally as much as 2,200 feet below sea level, is free from lavas. Some 30 miles southwest of Lake Kivu the lava field of South Kivu begins and extends to the southern and southwestern shores of the lake. After an interval the great lava field of North Kivu (Birunga), with two volcanoes still active, comes in at the northern extremity of the lake and extends over 40 miles northward and northeastward. Beyond the limits of this field there are sporadic occurrences of volcanic activity extending northward, with wide barren intervals, for a distance of 150 miles, to the southeastern foot of Ruwenzori. The activity in this section is characterized almost exclusively by explosion craters and tuff beds, lava flows being very rare.

The tuffs and other products of these northern vents are all potash-rich as are also nearly all the lavas of the North Kivu (Birunga) field. They are the best known lavas of the Central African Rift and it is this fact that has led to the acceptance of the rift as a region of potash-rich lavas.¹⁸ The latest flows of the latter area show, however, a distinct trend towards richness in soda. These occur at the southern extremity of the area, on the northern shores of Lake Kivu, into whose waters some recent lavas have poured, prominent among them being the Katerusi flow of 1912. Analyses have been made of a

¹⁵ Fuchs, V. E.: *Geogr. J.* London, 86, 126, 1935.

¹⁶ Terzaghi, Ruth Doggett: *This Journal*, 26, 377, 1935.

¹⁷ Fenner, C. N.: *Trans. Am. Geophys. Union*, 15, 241-243, 1934.

¹⁸ Holmes, A., and Harwood, H. F.: *Quart. J. Geol. Soc. London*, 88, 370-442, 1932, and *Geol. Survey Uganda Mem.* No. 3, pt. 2, 1937.

number of these flows with an excess of Na_2O over K_2O . They are given in Table II with references to the original papers. Included in the table is an analysis of the Kanamaharagi flow of 1905 which shows that the recent lavas do

TABLE II.
Analyses of Soda-Rich Lavas of North Kivu Lava Field.

	I	II	III	IV	V	VI	VII	VIII
SiO_2	47.67	44.42	48.62	46.71	44.18	44.82	37.70	44.88
Al_2O_3	14.20	14.27	17.44	12.46	14.77	18.11	13.83	14.22
Fe_2O_3	3.59	3.39	5.42	3.00	3.70	7.34	4.27	1.88
FeO	9.18	8.68	6.55	9.03	7.69	3.63	7.09	9.96
MgO	6.24	7.23	5.50	9.56	5.35	2.92	5.41	7.59
CaO	8.98	12.36	10.00	11.61	15.40	10.61	15.02	10.65
Na_2O	3.21	3.64	2.30	3.10	2.51	5.65	4.50	2.85
K_2O	2.41	2.44	1.92	1.06	1.02	4.30	4.92	3.09
$\text{H}_2\text{O} + \left. \begin{array}{l} \\ \end{array} \right\}$.92	.15	.63	1.11	1.13	.78	1.22	.08
$\text{H}_2\text{O} - \left. \begin{array}{l} \\ \end{array} \right\}$.09					.61	.03
TiO_2	2.64	3.42	1.29	1.74	2.19	.82	3.18	3.40
P_2O_5	.66	.13	.11	.33	.51	.78	1.86	.62
Cl0305
S050705
MnO39	.24	.26	.19
CO_212	.06
BaO05
	99.80	100.17	99.79	99.76	99.69	99.51?	99.99	99.65

- I Leucite basanite (doleritic), Mukira. L. Finckh, op. cit., p. 18.
- II Basanitoid, Bobandana. A. Lacroix, Min. de Madagascar, 3, 265, 1923.
- III Trachydoleritic leucite basanite, Kisenyi. L. Finckh, op. cit., p. 18.
- IV Limburgite, Adolph Friederich Volcano. L. Finckh, op. cit., p. 22.
- V Limburgite, Adolph Friederich Volcano. L. Finckh, op. cit., p. 22.
- VI Melilite nephelinite, Ngoma. L. Finckh, op. cit., p. 26.
- VII Melilite-leucite nephelinite, Ngoma. R. B. Ellestad, analyst.
- VIII Leucite basanite, Kanamaharagi. R. B. Ellestad, analyst.

not all have an excess of Na_2O , though the excess of K_2O in it is quite small. This lava, which is a leucite basanite and is named for its source, a small cone on the eastern slope of Nyamlagira, flowed to the lower slopes of Mikenno, destroying the banana groves of the natives. It has been examined microscopically by all who have studied collections from the area but has not hitherto been analyzed.

There is included in the table also an analysis by Hauser of a melilite nephelinite from the crater, Ngoma, a small crater

on the north shore of Lake Kivu. The analysis¹⁹ shows a considerable excess of soda over potash but there are in this case reasons for regarding the analysis as unacceptable. The rock is described as containing phenocrysts of melilite and nepheline in a groundmass consisting essentially of melilite and nepheline, with leucite, augite, magnetite and small amounts of other constituents. Yet the analysis of this rock, so rich in melilite, shows nearly 45 per cent SiO_2 (No. VI, Table II) and when the norm is calculated no calcium orthosilicate and no olivine is found. On the contrary there is over 25 per cent normative orthoclase and even some normative albite.²⁰ An analysis of a melilite-leucite nephelinite from Ngoma is now available (No. VII, Table II) which shows that the actual mineral composition of the rocks of this general type from the crater is not so notably abnormative. The norm, calculated from this analysis, shows no orthoclase or albite but much leucite and nepheline and more than 20 per cent calcium orthosilicate and olivine represented in the rock largely as melilite.²¹ It is clear that the Hauser analysis is not acceptable, indeed it may be noted that the summation of the analysis is given as 99.51 whereas the figures actually add up to 100.18, so that there is perhaps a printer's error involved. It is most unfortunate therefore that Holmes and Harwood should have used this analysis as representative of an actual rock corresponding with their hypothetical "Magma X" to which they attach fundamental importance in the genesis of rock types in the North Kivu area.²²

In contrast with the North Kivu lavas which show only in some instances a departure from the prevailing dominance of K_2O over Na_2O in the region of the Western Rift, the lavas of South Kivu, the southernmost area of vulcanism of this Rift, appear to trend towards a dominance of Na_2O , though there are marked exceptions to this condition. Unfortunately, not enough is known of their chemistry to permit a more definite statement.

At the time of our visit, little was known of the extent and general relations of the South Kivu field and we saw it for the

¹⁹ Finckh, L.: *Wiss. Ergebn. Deut. Zentral-Afrika-Exped.* 1907-8, 1 (1), 26, 1912.

²⁰ Washington, H. S.: *U. S. Geol. Survey, Professional Paper* 99, 583, 1917.

²¹ Bowen, N. L., and Ellestad, R. B.: *Am. Mineral.*, 21, 365, 1936.

²² Holmes, A., and Harwood, H. F.: *Geol. Survey Uganda Mem.* No. 3, pt. 2, 82, 1936.

most part only en route from Lake Tanganyika to Lake Kivu and on the shores of Lake Kivu itself. Since that time it has been discovered by Boutakoff²⁸ that the lavas of the South Kivu field came principally from two great composite volcanoes, Biega and Kahusi, to the southwest of Lake Kivu. From these centres flows spread as much as 40 miles to the south and southeast and 20 miles to the west. The most extensive flows are basaltic, though trachytes are rather wide-spread also. Of limited distribution and closely associated with the centres of eruption are masses of quartz porphyry and rhyolite which have emphasized explosive phases and the formation of Pelée-like domes. Of these various types only the basalts and trachytes were seen in our traverse.

The basaltic lavas have been described as ordinary olivine basalts but in specimens of adequately coarse crystallization it can be made out that there is a feldspar of index lower than balsam in the groundmass (anorthoclase) and the rocks would be more adequately described as trachydolerites, indeed their general microscopic aspect is trachydoleritic. A specimen collected at the rapids at the outlet of Lake Kivu appears to be typical. It has phenocrysts of augite and olivine in a groundmass containing the same minerals with labradorite. This is zoned and passes to anorthoclase which is not abundant but forms a sort of mesostasis. Specimens of columnar lava from the shores of Lake Kivu about a mile northwest of Bukavu (Costermansville) are not significantly different. By reason of a mislaying of the specimens after chips had been sent off for thin sections it has not been possible to get an analysis of these trachydoleritic basalts. They show no significant microscopic differences from the trachydolerites of the North Kivu field but whether they would prove to be potash-rich or, on the other hand, soda-rich, like the basaltoid rocks of the Eastern Rift is a question that has not been decided.

The trachytes are light-colored rocks and have not been described in detail hitherto. Two specimens of somewhat different character have therefore been selected for analysis and special description. One of these was collected by Professor Willis one mile west of the road at a point 3 miles south of Costermansville and at an elevation of 600 feet above the lake. It is a highly vesicular lava of a light, ash-grey color, with rare phenocrysts of feldspar. Microscopic examination shows

²⁸ Boutakoff, N.: Bull. soc. belge géol., 43, 42, 1933.

that these are of andesine, about Ab_1An_1 ($\gamma = 1.550$), mantled by alkali feldspar, and reveals other smaller phenocrysts of basaltic hornblende and more rarely of alkali feldspar. The hornblende is pleochroic from amber to deep brown. It has the refractive indices $\gamma = 1.719$, $\beta = 1.700$ and $\alpha = 1.686$. The extinction angle $c \wedge \gamma = 3.5^\circ$. These hornblendes have been changed peripherally, and sometimes through and through, to a fine-grained aggregate rich in magnetite, a change which attests the instability of the hornblende in contact with magma under surface or near-surface conditions. The groundmass is made up principally of laths of alkali feldspar with prisms of the same brown hornblende, of aegirine-augite, apatite and grains of magnetite.

The chemical composition of the rock is given in Table III. It is that of a trachyte. The norm shows some 11 per cent of

TABLE III.
Analyses of Soda-Rich Lavas of South Kivu Lava Field.

	I	II	III		I(a)	II(a)
SiO ₂	57.45	60.29	58.89	Q	3.2	5.8
Al ₂ O ₃	19.46	19.55	17.61	or	24.5	31.1
Fe ₂ O ₃	4.65	3.60	2.44	ab	46.1	48.2
FeO	.91	.60	3.47	an	11.4	1.1
MgO	1.18	.50	.65	C	1.8	4.0
CaO	2.99	.61	2.11			
Na ₂ O	5.47	5.68	4.57	hy	3.0	1.2
K ₂ O	4.11	5.33	7.86	il	2.1	1.5
H ₂ O+	1.21	1.77	1.80	hm	4.6	3.7
H ₂ O—	.42	.50		ap	1.3	.7
TiO ₂	1.26	.84	.58	rutile	.2	.2
P ₂ O ₅	.55	.27	.11			
MnO	.12	.16	...			
	99.78	99.70	100.09			

- I Trachyte, 3 miles south of Costermansville. R. B. Ellestad, analyst.
 II Trachyte, at outlet of Lake Kivu. A. Willman, analyst.
 III Trachyte Karisimbi (North Kivu) for contrast. L. Finckh, op. cit., p. 4.
 I(a) Norm of I.
 II(a) Norm of II.

anorthite from which fact, together with the presence of phenocrysts of andesine, the rock may be regarded as transitional toward trachy-andesite.

The other trachyte was collected near the outlet of Lake Kivu. It is a compact ash-grey type, free from gas pores and showing rare, small phenocrysts of feldspar. Under the micro-

scope these phenocrysts prove to be albite-oligoclase ($\gamma=1.542$) and the groundmass is found to be very rich in laths of alkali feldspar with some aegirine-augite passing to aegirine, an alkali hornblende, pleochroic from yellow to brown that may be called barkevikite, apatite needles, magnetite grains and probably quartz. The chemical composition of the rock is given in Table III. It is typically trachytic. The normative anorthite is only 1 per cent. It should be mentioned that the exact field relations could not be made out. The compact, non-vesicular character suggests that the mass may be a dike or neck rather than a flow, a possibility that is further indicated by an ill-defined vertical sheeting. If it is a dike it would be appropriately named bostonite.

These rocks contain a significant excess of Na_2O over K_2O and are thus strongly contrasted with trachytic types from North Kivu. The analysis of a trachyte from Karisimbi is given for comparison. The South Kivu trachytes are more closely related to rocks of the Eastern Rift. It is true that rocks of the Eastern Rift usually contain an excess of alkalis over Al_2O_3 , whereas the rocks just described exhibit the opposite relation, having some corundum in the norm. But this condition is not unknown in rocks of the Eastern Rift especially among the more salic types. Thus the quartz bostonite described by Lehmann²⁴ from the Rungwe area has some normative corundum, and one of the obsidians of the Naivashan area has also a small amount.²⁵

It is especially to be noted that the sodic trachytes of the South Kivu area are not contemporaneous with the very late lavas of similar alkali trend in the North Kivu area. On the contrary the former are deeply weathered, erosion has imposed upon them mature land forms, and they are probably among the oldest products of vulcanism in the Western Rift.

In the South Kivu lava field there are in addition to the types above described some lavas of salic character which have a very unusual chemical composition. These have been described by Sorotchinsky.²⁶ They comprise rhyolites of excessively high SiO_2 content (84 per cent), quartz porphyries high in K_2O (7.58 per cent) and poor in Na_2O (.32 per cent), other remarkable rhyolites with upwards of 30 per cent mag-

²⁴ Lehmann, E.: *Z. Vulkanologie*, 4, 113, 1924.

²⁵ Bowen, N. L.: *This Journal*, 33, 15, 1937.

²⁶ Sorotchinsky, C.: *Mém. inst. géol. univ. Louvain*, 9 (vi), 98, 1934.

netite and yet others with notable amounts of graphite. Sorotchinsky interprets these as the result of fusion of subjacent formations but the extraordinary chemical characters noted are strongly suggestive of hydrothermally altered lavas. Numerous thermal-mineral springs are shown on the map of the area.

It is clear from the above discussion that the rocks of the Western Rift, while they in general show a moderate dominance of K_2O over Na_2O , nevertheless depart from that relation in many instances and thus render it impossible to accept any simple chemical picture of the Western Rift which one might hope to connect with tectonic influences. Indeed when we come to examine the detailed studies of the petrogenesis of these potash-rich African rocks we find that much evidence has been adduced pointing to a relatively accidental origin of this chemical character. Finckh²⁷ in his early studies of the North Kivu rocks pointed to inclusions of biotite pyroxenite in some of them, which inclusions had been partly converted to glass. To this glass biotite made the principal contribution and it is, therefore, rich in K_2O . Holmes and Harwood²⁸ in their recent study of the rocks of the same area have also attached great importance to the reaction of magmas with biotite pyroxenite inclusions (transfusion) and have decided that the original magma or magmas of the area showed a dominance of Na_2O over K_2O typified in their "Magma X." Their choice of an actual rock representative of "Magma X" has, as we have seen, not been fortunate, nevertheless my own studies of the rocks of the North Kivu area have led me to the conclusion that the contamination of a soda-rich magma by selective reaction with biotite pyroxenite is one possible explanation of the origin of potash-rich types in that area.

It may be suggested that the old sodic trachytes of South Kivu, and the associated trachydolerites, are representative of the original characters of the early magmas; that in later activity, especially in the northern areas, these magmas suffered contamination of the kind described and that this effect is now waning and the magmas, as represented in current activity in North Kivu, are reverting to their original sodic character. In this view there is no reason for connecting the potash-rich

²⁷ Finckh, L.: op. cit., p. 31.

²⁸ Holmes, A., and Harwood, H. F.: Geol. Survey Uganda Memoir No. 3, pt. 2, p. 82.

lavas with any particular kind of crustal movement. If there is any connection between magma chemistry and tectonics it would appear that the control has on the whole been such as to make the lavas *normally* soda-rich throughout the Rift systems.

CONCLUSIONS.

As we have pointed out, many investigators have believed that sodic rocks are connected with crustal foundering. Such connection cannot, however, always be substantiated though the tendency toward frequent occurrence of soda-rich rocks in regions of foundering, or what has all the appearance of foundering, seems reasonably clear. One might, then, be tempted to urge that the *normally* soda-rich character of the Rift lavas indicates that the Rift Valleys are formed as a result of foundering, foundering which has followed an uplift, of course, for presumably no one doubts the general uplift of the African continent. It is, however, a temptation easy to resist. When we are still uncertain that there is any connection between tectonics and magma chemistry, when we are still uncertain as to whether what is called foundering is anywhere due to lack of adequate support, as the word implies, or whether it is only apparently so and is really a down-pressing, or again is neither, but rather a lagging behind in a general uplift—when we are uncertain of all these things it is easy to refrain from drawing the conclusion that the chemistry of African lavas favors any particular concept of the mechanism of Rift formation. In addition there is little encouragement to consider the relations observed in the African continent as an unequivocal demonstration of the control of tectonic forces over the composition of igneous magmas.

THE PHENOMENA OF FALLING MOUNTAIN.

CLARENCE N. FENNER.

ABSTRACT.

At the time of the volcanic eruptions in the Katmai country, Alaska, in 1912, one of the effects of the accompanying disturbances was the breaking off of an enormous mass of rock from the face of a mountain at the head of the Valley of Ten Thousand Smokes. When the Valley was first explored, in 1916, and for many years afterward, the shattered face of the cliff was the site of fumarolic activity, intense at first and gradually diminishing. During this same period, masses of rock, some of great size, continued to break away from the cliff and accumulate at the bottom.

Evidence is given that the rock of the mountain had originally been a rather siliceous andesite, whose appearance was not extraordinary, but examination of the rocks of the talus pile, derived from the cliff that was being subjected to the action of fumarolic vapors, shows that remarkable features had been developed. Many of the blocks were riddled with large and small channels and irregular cavities. A profusion of tridymite crystals had been deposited, and a smaller amount of cristobalite and hematite.

From the close interrelationship that the phenomena seem to display, it is believed that the formation of the penetrating passages, as well as the deposition of secondary minerals, was due to the fumarolic gases. A remarkable demonstration of such action seems to be presented.

A rather spectacular feature of the Valley of Ten Thousand Smokes, in the Katmai National Monument, is that to which the name of Falling Mountain has been given. Prof. R. F. Griggs, leader of the National Geographic Society Expedition that first entered the Valley, and of subsequent expeditions, has written as follows concerning it:

"Whenever it has been under observation, ever since its discovery in 1916, this rock face, which we named Falling Mountain, has been subject to frequent avalanches. The constancy of their occurrence is one of the most impressive features of the Valley.

"The falls of rock vary all the way from single boulders up to large masses weighing many tons, which let go with a crash distinctly audible for miles around. During the first two seasons, a five-minute period never passed without a fall of some sort, but in 1919 the mountain was often quiet for half an hour at a time."¹

The present writer was a member of the National Geographic Society Expedition of 1919, and in 1923 made a second visit

¹Griggs, R. F.: *The Valley of Ten Thousand Smokes*, The National Geographic Society, Washington, p. 241, 1922.

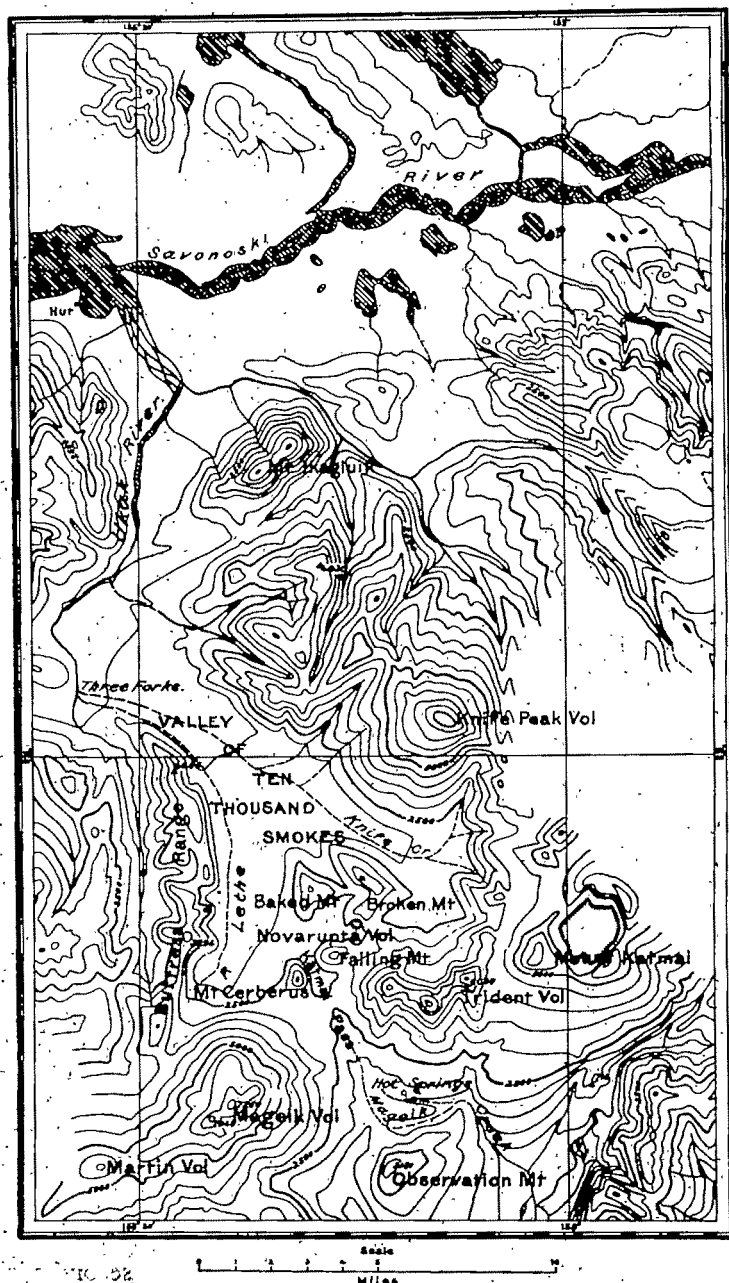


Fig. 1 Map of the Valley of Ten Thousand Smokes and its vicinity.

to the region on an expedition sent out by the Geophysical Laboratory of the Carnegie Institution. On both occasions studies of the mountain and of its rocks were made, in an endeavor to determine the cause of the avalanching. Short descriptions of pertinent features have been given in several articles.²

In the writer's article of 1920 the statement was made:³

"Apparently the gases that permeate the rocks and that manifest themselves at the surface by the slowly rising vapor clouds are capable of reacting with the constituent minerals in such a way as to form volatile compounds, and the porosity indicates that quantities of material have actually been removed by gaseous transfer."

The nature of the phenomena on which this statement was based deserves more detailed description. Later study seems to confirm the conclusion, and an unusually clear-cut case of the corrosive and transporting power of magmatic gases seems to be presented.

The subject of gaseous transfer is recognized by geologists as of much importance, but considerable difference of opinion exists respecting it. Some geologists incline to the view that the gases have this power in large measure, whereas others are inclined to believe that any important transporting effects attributable to the influence of magmas are due to the circulation of heated waters rather than gases.

The position of the mountain with respect to other features of the vicinity is shown on the map, Fig. 1, and a photograph of the broken scarp, viewed from the north, appears in Fig. 2, taken in 1923. Figure 3 is a view from the northeast, showing the prolongation of the system of fractures that shattered the face of the mountain, extending far to the left of the scarp. A little fumarole action along these cracks is visible. Other illustrations may be found in Griggs' book, *The Valley of Ten Thousand Smokes*.⁴

² Fenner, C. N.: *The Katmai Region, Alaska, and the great eruption of 1912*, J. Geol., 28, 569, 1920.

Fenner, C. N.: *The origin and mode of emplacement of the great tuff deposit of the Valley of Ten Thousand Smokes*, Nat. Geog. Soc., Contrib. Tech. Papers, Katmai series, No. 1, 1923.

Fenner, C. N.: *Earth movements accompanying the Katmai eruption*, J. Geol., 33, 116, 1925.

³ Op. cit., p. 586.

⁴ Op. cit., pp. 202 and 280.



Fig. 2. The shattered cliff of Falling Mountain, seen from the north, at a distance of about a mile. Photo taken in 1923.



Fig. 3. Falling Mountain, from the northeast, showing prolongation of fractures beyond the scarp of the cliff. Mount Mageik in background. Photo taken in 1923.

In order to give the reader a sufficient background of information for what follows, a brief outline of what we believe to have been the sequence of events of the eruption of 1912 will be presented.

Before the violent outburst in the crater of Mount Katmai occurred, a sill or offshoot of rhyolitic magma from the main body was injected between the nearly horizontal strata that underlie the Valley of Ten Thousand Smokes. In most places the area under which the magma was injected coincided closely with the area of the Valley. This was probably due to the fact that the strata of the roof yielded to mechanical uplift much more readily in the Valley area than in contiguous places where they were subjected to the additional weight of the steep mountains that bound the Valley. At the head of the Valley, however, mountainous slopes intervened between the source of the injection, in the neighborhood of Mount Katmai and Mount Trident, and the area of the Valley to the northwest. Forcible injection beneath this intervening mountainous country caused many breaks and dislocations of the roof, and these outlets became the site of numerous fumaroles on the lower slopes of Trident, and on neighboring eminences (see illustration on page 194 of Griggs' book). Near the head of the Valley stand Broken Mountain and Falling Mountain. On Broken Mountain, faults of large displacement are visible. At Falling Mountain, the main mass of the eminence was probably not greatly disturbed, but a slice of the outer face was broken off in a great avalanche. The appearance of the mountain leaves no doubt that this break occurred; nevertheless the enormous mass of material has totally disappeared from view. It has been covered by the incandescent sand flow, which formed the second major episode of the eruption.

The sand flow is believed to have been a great flood of fragmental material, derived from the gaseous vesiculation and comminution of portions of the magma that rose to the surface through many breaks in the shattered roof overlying the injected sill. For a number of years after the discovery of the Valley, the sites of these fissures were marked by lines of fumaroles throughout the area of the Valley, but in most places these have subsequently disappeared. The great thickness of sand-flow material in the vicinity of Falling Mountain is attested by the complete burial of the rock of the avalanche.

The sand flow was followed by explosive activity of considerable magnitude at the new crater of Novarupta. This sub-

sidiary volcano was situated about a mile to the north-northeast of Falling Mountain, and its outburst was doubtless another manifestation of the release of gas-charged magma from the underlying intrusion. At about the same time, great explosions began in the main crater of Katmai, six or seven miles to the east. With these the present article is not concerned, except in the fact that in all phases of the eruption the action of a highly gas-charged magma is indicated. After the violent manifestations subsided, a continued evolution of gases for many years was seen in the fumaroles of the Valley area, as well as in those of Novarupta, those of the lower slopes of Mount Trident, and those of the shattered cliff of Falling Mountain. A photograph on page 202 of Griggs' book shows intense fumarolic activity on a portion of Falling Mountain in 1916. Figure 4 of the present article, taken by the writer in 1923, represents almost the same area, but vapors then issued in much diminished quantity.

The observations made by the writer in 1919 were as follows: The face of the cliff was a precipitous slope. The upper parts were of rock; the lower were talus slopes, with a large accumulation of talus at the foot. At intervals of a few minutes, rocks broke away from the upper face and crashed down, reaching nearly or quite to the bottom. The frequency and unpredictability of rock falls prevented any thought of climbing the cliffs, and watchfulness was advisable in examining the rocks of the talus piles.

From numerous places on the face, from bottom to top, vapors were issuing. Just at the foot of the talus piles there were trenches and crater-like depressions, 15 feet or so deep, from which steam likewise issued. The trenches were due in large part to the intersection of craters along lines parallel to the foot of the mountain. Craters and trenches probably marked the surface trace of the zone of fracturing that caused the shattering. A view of one of the craters, as it appeared in 1923, is shown in Fig. 5. In the latter year, examination of the upper, well-stratified layers of pumice and rock shown at the right of this photograph indicated that they were localized around the craters and had been formed by secondary explosions, by which loose material had been blown out of vents situated along the fissure. In these strata of ejecta, angular blocks of unaltered andesite of Falling Mountain were present. The presumption is that such ejected blocks, in their present situation, were derived from buried portions of the Falling

Mountain avalanche. Their unaltered condition is regarded as important evidence of the fact that at the time of the avalanche



Fig. 4. Eastern end of the cliff of Falling Mountain, with vanishing fumarolic activity in 1923.

the rocks of the mountain had not yet been affected by the fumarolic action that later altered so greatly the rocks of the cliff.

In 1919, the upper slopes were seen to be in a shattered condition, and great boulders that had reached the bottom had partly broken down into fragments. Two of these masses, at that time, were especially remarkable. They formed cones, probably 50 feet high, with relatively solid cores, surrounded by piles of fragments that had broken off from them. Other masses were similar, but they were smaller, or the cone shape



Fig. 5. One of the craters of secondary explosion at foot of Falling Mountain. The upper strata at the right are localized deposits adjacent to the vent and dip away from it. They represent material blown out by explosions. Photo taken in 1923.

of the *débris* was not so prominent. One of the larger masses consisted of purplish andesite, penetrated by apparent solution channels, and so cellular in places as to be almost a scoria. The cavities were lined with tridymite crystals. The numerous irregular channels, piercing the mass of what had seemingly been at one time solid rock; the profusion of tridymite crystals; and the derivation of the block from the cliff face through which fumarolic vapors were being discharged, seemed to point to the gases as the agency that had formed the channels.

From numerous orifices in this detached mass, steam was issuing. It had a slight odor, difficult to define, but suggestive of organic material (perhaps derived from the sedimentary strata beneath). Around these vents the rock was reddened, and thin crusts of light gray, yellow, and green material were found. It was evidently impossible that the issuing vapors

should have originated in the mass itself, and it was supposed that they came from a source far below, and happened to find outlet through the cavities of the rock. They demonstrated how thoroughly the mass was riddled. At the base of the cone, there was an irregular crater, from which steam issued in large volume.

The talus slopes at the foot of the cliff were composed predominantly of light purple to purplish gray blocks, and in vugs in these, large quantities of tridymite crystals again were found. The purplish color was evidently due to the oxidation of the iron of the rock. The pyroxene phenocrysts were more or less replaced by aggregates of hematite. Unaltered rock was light gray in color.

In occasional talus blocks, rather obscure flow-banding was seen. Some blocks contained fairly numerous, angular xenoliths, similar to the rock of the matrix.

The spalling off of quantities of fragments from the masses after they had reached the bottom of the slope was curious. It may have been related to another phenomenon of the following character, noted by a number of observers, including the writer. Rock falls from the face of the cliff were distinctly less numerous in the early hours of the morning than later in the day. It seemed as if diurnal changes of temperature had a decided effect in causing blocks to break loose from the cliffs, and perhaps in the disintegration of fallen masses of rock, but the reason why changes of temperature should have had this effect is not clear. The formation of secondary minerals had doubtless set up strains within the masses of rock, and possibly the repeated diurnal changes developed cracks that finally caused rupture. The disintegration of fallen masses did not continue indefinitely, for in 1923 several of the larger ones appeared to be in about the same condition as in 1919. They are visible on close examination in Fig. 2.

Rock falls from the cliff were less frequent in 1923 than they had been in 1919, and vapors issuing from the cliff face had diminished. In 1930, Griggs made another visit to the region, and he has kindly supplied the following information:

"The period [during which he was encamped near Falling Mountain] was from July 3 to July 9. At that time, Falling Mountain was entirely inactive, though there may have been an occasional rolling rock but no more than would occur on any

cliff in the region. The little fumaroles high up on the mountain were still there although smaller than when I saw them in 1919. The word 'inactivity' seems to sum up the situation."⁵

The account that has been given brings out certain points to which it is desired to direct attention. When the mountain was first seen, four years after the eruption, masses of rock were frequently falling from the cliff, and fumarolic vapors were leaking through the shattered face in large quantity. Three years later, in 1919, both effects had subsided considerably. Four years after that, in 1923, a further diminution was noticeable, though there was still some activity in both respects. After 18 years, in 1930, almost nothing of significance was occurring.

It does not seem likely that the primary shattering, viewed as a mechanical disturbance, caused effects that continued to manifest themselves for more than 11 years. At other places in the Katmai region great cliffs broke away during the eruption, but no similarly prolonged after-effects were observed. The continuance of the rock falls at Falling Mountain were evidently due to a cause that was itself continuing. This points to the fumarolic vapors as the only agency that seemed to continue in operation.

The broken face of Falling Mountain is about 1,400 feet high. The origin of the mountain itself is somewhat of a puzzle. Most of the rock of the talus has been altered, and oxidation of iron has given it a purplish tone, but the least altered rock is a dense, light gray, siliceous andesite, in which numerous phenocrysts of pyroxene (mostly orthorhombic, and of negative optic character) and plagioclase are set in a groundmass of much finer grain. The texture is not inappropriate for a lava flow, but the great thickness of uniform-looking rock, with only obscure banding and without other conspicuous structure, is not altogether in accord. On the west side of the entrance to Katmai Pass is a similar conical eminence, Mount Cerberus, composed of similar rock. The peaks of the two are a little more than a mile apart. The question of what those two peaks represent, in terms of origin, is an interesting problem, but it is immaterial for the present study.

The talus accumulation on the lower slopes and at the foot of the shattered cliff is of large size, but it is insignificant in

⁵ Griggs, R. F.: Personal communication.

comparison with the quantity of material that disappeared. A description of the character of the boulders, as examined on the ground, has been given. Typical specimens were collected for subsequent laboratory study. It was difficult to find any rock in which tridymite crystals could not be seen with a hand lens, and in which pyroxene phenocrysts had not been oxidized to hematite. A specimen selected as relatively unaltered gave the analytical results of Table I.

TABLE I.
Analysis of A 147, a relatively unaltered andesite from
Falling Mountain.

SiO ₂	65.51
Al ₂ O ₃ *	15.79
Fe ₂ O ₃	1.71
FeO	3.50
MgO	2.15
CaO	4.88
Na ₂ O	4.03
K ₂ O	1.64
H ₂ O	0.01
TiO ₂	0.56
MnO	0.07
	<hr/>
	99.85

* Includes P₂O₅.

The collected specimens show interesting and significant phenomena, similar to those seen on the ground. Many of them are penetrated by solution channels, and minerals of the sort that one would expect as a result of the passage of magmatic vapors have been deposited. The channels vary greatly in size. A considerable portion of a specimen may be penetrated by minute cavities, passing down to microscopic dimensions. Some of the larger of these are narrow and slightly elongated. Evidently the solvent medium had been guided by a crack or flaw, though now their sides are irregular and do not match. Many are simply holes. Cavities of much larger size also are present. In their typical form, they are extremely irregular. They may consist mostly of open space, or may have a loose structure that might be called spongy, though this implies more regularity than is present. All surfaces are covered with a rough coating of drusy tridymite crystals, which adds to the irregularity. The spongy-looking masses might appear, at first sight, to have been a rubble produced by crushing, and subsequently corroded by solution, and

finally covered with a deposit of tridymite. Crush breccias were probably formed in places by the original shattering, but a more general effect was probably the formation of flaws or incipient cracks, which directed the passage of corrosive vapors. In most specimens the irregularity of the cavities is plainly an effect of solution rather than brecciation, as shown by the fact that, in general, cavities are not extended along a plane or zone, and prongs projecting from the sides, however uneven their forms may be, are attached to the walls. Corrosion seems to have been the predominant process. When thin sections of specimens that are characterized by large or small cavities are studied microscopically, the whole rock is found to be impregnated with tridymite.

Tridymite is the characteristic mineral of these altered rocks. Most of it is in the form of thin plates, which are of small dimensions but are recognizable with a pocket lens. In addition, the cavities have a sparse sprinkling of little equant grains, $\frac{1}{4}$ to $\frac{1}{2}$ mm. in dimensions, that are white and porcelain-like. These have been found to be cristobalite. They have somewhat irregular but definite crystal faces, which might be identifiable with a goniometer. They were evidently deposited as isometric crystals, which broke up into aggregates on cooling through the inversion temperature.

The pyroxene phenocrysts have been altered to hematite, which may replace the phenocrysts completely or may leave unaltered cores. In addition, a dust of numerous but very tiny plates of hematite has been deposited.

Analysis of a specimen, altered in the manner described, is given in Table II.

TABLE II.

Analysis of A 138, a specimen of altered andesite from
Falling Mountain.

SiO ₂	65.01
Al ₂ O ₃ *	16.22
Fe ₂ O ₃	4.77
FeO	0.60
MgO	1.86
CaO	5.30
Na ₂ O	3.76
K ₂ O	1.56
H ₂ O	0.08
TiO ₂	0.64

 99.80

* Includes P₂O₅.

In this analysis, the oxidation of pyroxene is shown in the large ratio of Fe_2O_3 to FeO . Otherwise the percentages are not greatly different from those of the less altered specimen. The most significant difference is the increase of CaO in respect to alkalis. This is probably to be attributed to the phenocrysts of feldspar having been more resistant to attack than the feldspars of the groundmass. That seems to be a common characteristic of feldspar phenocrysts, in alteration either by aqueous solutions or by gases.

The fact that the two analyses do not differ greatly from each other is, of course, not an indication that no large quantity of material was carried away by the solvent medium: the large cavities and smaller channels that pierce the rock demonstrate the contrary. The similarity of analyses shows that the constituents were dissolved in approximately the proportions in which they had originally been present.

SUMMARY AND CONCLUSIONS.

At the beginning of the eruptive period a large slice of the face of Falling Mountain was broken loose and collapsed into the valley below. Presumably portions of the cliff left standing were somewhat fractured at the same time, and were rendered permeable to magmatic gases that were evolved from the subterranean magma. These gases appeared at the surface as copious fumarolic exhalations, which continued for several years. During the same period, masses of rock continued to fall from the cliff face, and accumulated in a talus pile at its base.

Examination of the rocks of the pile shows them to contain large quantities of minerals of the sort that pneumatolytic processes are likely to produce. The most plentiful of these minerals is tridymite, but cristobalite and hematite also were formed in considerable quantity. The rocks have become riddled with solution channels, and large amounts of mineral constituents have been carried away. Prior to the shattering of the cliff, the rock seems to have been a dense andesite in unaltered condition.

The close correspondence in time between the period of fumarolic activity and that of rock falls indicates a relation of cause and effect, and the alteration of the rock was of a nature that was well fitted to cause disintegration of the cliff.

If we may accept what seems a logical interpretation of the

evidence, we recognize that solvent and mineralizing processes of considerable magnitude were brought about by magmatic vapors acting upon the rocks of Falling Mountain. The quantity of mineral matter carried away was large. The conditions were such that the possibility of the action of aqueous or aqueo-igneous liquids during the period of alteration seems to be excluded. A feature that it is important to recognize is that solution of rock material was not confined to such constituents as alkalis and iron, which form easily volatile chlorides and might be expected to be carried away in much the greatest amounts, but that it included in its action all the material of the rock. Solution in the gaseous medium produced open spaces, large and small, from which everything has been removed.

ON THE EFFECT OF PRESSURE ON THE SOLUBILITY OF SOLIDS IN LIQUIDS.

R. E. GIBSON.

ABSTRACT.

From an empirical analysis of the data concerning the effect of pressure on the solubility of solids in liquids, the volume changes and compressibilities of solutions, it is concluded that only in somewhat exceptional cases is the solubility of a solid in a liquid raised by pressure, a conclusion which is not novel. However, solutions of the carbonates, sulphates, sulphides, fluorides, and hydroxides of some alkalis, the alkaline earths, and the heavy metals in water, especially where the saturated solutions are very dilute, are definitely to be classed among these exceptional cases, and it is pointed out that the solubilities of these substances may be very significantly increased by pressures below 1000 atmospheres. It seems unlikely that the solubility of silicate minerals in molten silicates will be increased by pressure, and, indeed, the opposite effect is more to be expected, although the complications introduced by structural effects in these liquids render general statements quite risky.

The empirical arguments leading to these conclusions are given in some detail and especial emphasis is laid on the volume change which takes place when the liquid components are mixed, a quantity which at low pressures plays an important rôle in determining the piezochemical behavior of poly-component systems and sometimes renders deductions based solely on the thermodynamic behavior of the pure components inapplicable to solutions. The effect of pressure on the solubility of solids is correlated qualitatively with the types of cohesive forces in the pure components and the solutions involved.

New data on the solubility of cesium bromide in water at pressures up to 1500 atmospheres and the partial volumes of sodium chloride at 1 and 1000 bars pressure and at temperatures between 25 and 95° C. are also included.

INTRODUCTION.

The influence of pressure on the solubility of solids in liquids is of special interest in any study of naturally occurring solutions such as molten silicates or aqueous solutions of sparingly soluble substances, where one part of the problem requires a knowledge of the conditions under which a solution and a number of solids exist at equilibrium under the high pressures prevailing at moderate depths below the surface of the Earth.

In the last two decades it has been found experimentally that the solubilities of solids in water and other solvents may be altered very significantly by pressure changes of a few thousand atmospheres. The pressure-solubility curves that are available for binary systems, however, are of all possible types, and superficially, at least, show few regularities in behavior.

For example, the solubility of sodium chloride in water¹ rises slightly with pressure, passes through a maximum, and then slowly decreases at the highest pressures; the solubility curve for potassium sulphate² in water is similar in shape but the changes in solubility are very much larger. The solubility of ammonium nitrate³ in water falls as the pressure is raised, decreasing steadily from 67.6 per cent at 1 bar (approximately an atmosphere) and 25° C. to 29.7 per cent at 10,000 bars. In Table I we give new data for the solubility of cesium bromide

TABLE I.

The solubility of cesium bromide in water at 25° and different pressures.

Pressure (bars)	Grams of CsBr per 100 grams of water
1	123.7
505	117.9
1010	111.9
1510	106.8

in water at different pressures. These solubilities were measured directly by the method of Adams and Gibson,⁴ and the results are similar to those for the ammonium nitrate-water system. On the other hand, the solubility of potassium iodide⁴ in water increases with pressure up to 10,000 bars, the solubility of zinc sulphate heptahydrate in water is lowered, while that of cadmium sulphate octotritrahydrate⁵ is raised by pressure. The solubility of barium hydroxide⁶ increases rapidly with pressure in the short range that has been studied.

Analysis of these results, and of a large number of results of determinations of the compressibilities and volume changes on mixing of solutions of salts in water and other solvents does, however, reveal certain regularities which render possible predictions as to the sign and approximate magnitude of

¹ Adams, L. H.: *J. Am. Chem. Soc.*, 53, 3769, 1931.

² Adams, L. H.: *J. Am. Chem. Soc.*, 54, 2229, 1932.

³ Adams, L. H., and Gibson, R. E.: *J. Am. Chem. Soc.*, 54, 4520, 1932.

⁴ Gibson, R. E.: *J. Am. Chem. Soc.*, 56, 865, 1934.

⁵ Cohen, E., and Sinnige, L. R.: *Z. phys. Chem.*, 69, 102, 1909.

⁶ Sill, H. F.: *J. Am. Chem. Soc.*, 38, 2632, 1916.

the change of solubility with pressure in certain types of solutions. The object of this paper is to give some recent results of such an analysis, to relate the effect of pressure on the solubility of solids in liquids to measurable properties of the pure components and of the solutions involved, to give some new examples particularly of the effect of temperature changes, and to present some conclusions of general interest.

THERMODYNAMIC CONSIDERATIONS.

We may begin this discussion with the thermodynamic formula which gives exactly the variation of composition with pressure which must be obeyed if a solid and a solution are to coexist in equilibrium. This may be written as follows:⁷

$$\frac{dx_2}{dP} = - \frac{v_2 - v_2^s}{(\partial \mu_2 / \partial x_2)_{P, T}} \quad (1)$$

where x_2 is the composition of the saturated solution, P is the pressure, v_2 is the partial volume of the solute in the solution, v_2^s its specific volume in the solid phase, and $(\partial \mu_2 / \partial x_2)_{P, T}$ is the rate of change of the chemical potential of the solute in the solution with change of concentration at the temperature and pressure of the experiment. It follows directly from the two laws of thermodynamics that $(\partial \mu_2 / \partial x_2)_{P, T}$ must always be positive, and hence dx_2/dP is positive if $(v_2 - v_2^s)$ for the saturated solution is negative and negative if $(v_2 - v_2^s)$ is positive,⁸ that is to say, pressure will increase or decrease the solubility of a solid according to whether $(v_2 - v_2^s)$ is negative or positive and it becomes of interest to see how the various chemical and physical properties of the pure components and of the solution influence the sign of $(v_2 - v_2^s)$.

In Fig. 1 we have plotted $(v_2 - v_2^s)$ as a function of the concentration for a number of different solutions at room temperature. These values were calculated from direct

⁷ This expression holds for a pure solid, i.e., one of invariant composition in equilibrium with a binary solution. The complete expression, taking into account the possibility of solid solution, is given by Adams: Ref. 1, p. 3803.

⁸ As $(v_2 - v_2^s)$ is exactly the volume increase when 1 gram of the solid dissolves in an infinitely large amount of the saturated solution, we see that equation (1) is a quantitative statement of the Le Chatelier-Braun theorem. Equation (1), however, was given in substance by Gibbs many years before the qualitative theorem was rediscovered.

measurements of the specific volumes of solutions and illustrate how $(v_2 - v_2^*)$ depends on the concentration of the solute in the solution, the compressibility of the solvent, and the

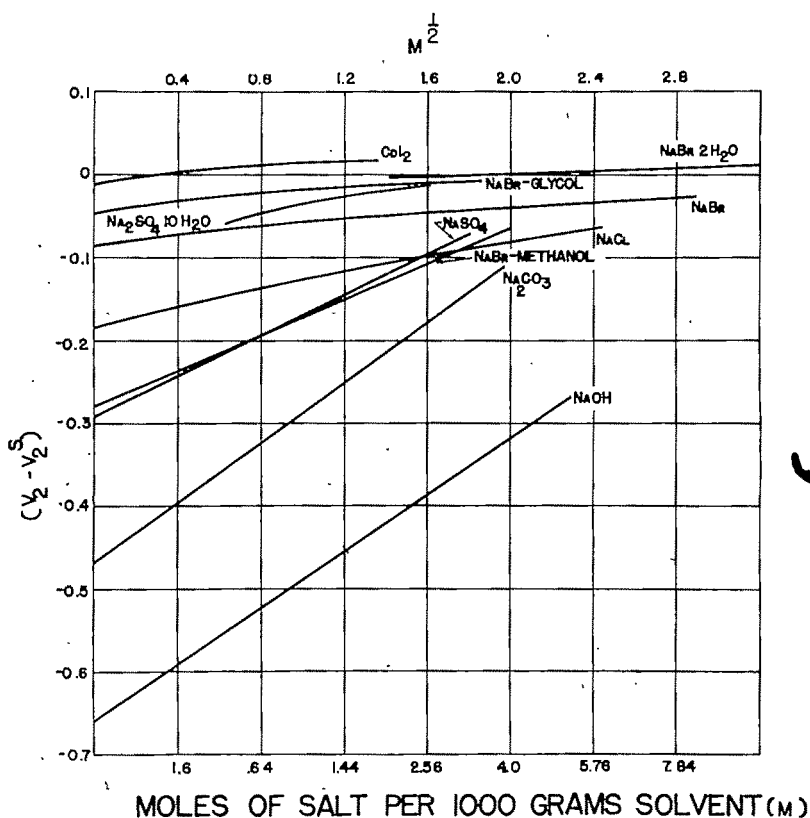


Fig. 1. The expansion in milliliters per gram of different solids when they dissolve in solutions of different concentrations. Unless otherwise stated the solvent is water. Comparison of the curves for sodium bromide in methanol, water, and glycol illustrates the effect of the compressibility of the solvent. Note that in all the dilute solutions the expansion is negative.

chemical nature of the solute.⁹ A general discussion of the factors influencing $(v_2 - v_2^*)$ is complicated by the fact that when a solid dissolves in a liquid, two distinct processes occur—the solid melts with a given volume change and the liquefied

⁹ At 25° the compressibilities of glycol, water, and methanol are respectively 36.6, 44.5, and 125×10^{-6} reciprocal bars.

solute mixes with the solvent with another volume change. We should, therefore, write $(v_2 - v_2^*) \equiv (v_2 - v_2^1) + (v_2^1 - v_2^*)$ where v_2^1 is the hypothetical volume of the pure liquefied solute at the temperature and pressure of the experiment, and then discuss separately the volume change on melting $(v_2^1 - v_2^*)$ and the volume change on mixing $(v_2 - v_2^1)$. It will be shown that this latter term plays an important part in determining the effect of pressure on equilibria in many binary systems. Indeed, the volume change on mixing term is so significant that its consideration may require a complete revision of conclusions about the behavior of polycomponent systems under pressure that have been based on careful considerations of the thermodynamics of pure substances.¹⁰

THE VOLUME CHANGE ON MELTING OF SOLIDS.

Most substances expand on melting, $(v_2^1 - v_2^*)$ being, therefore, positive. Exceptions are known at low pressures, notably water, bismuth, and perhaps potassium nitrate and potassium and rubidium iodides,¹¹ but Bridgman¹² has found that at higher pressures such substances frequently undergo polymorphic transitions and thereafter melt with increase in volume. At high pressures, therefore, it is very exceptional to find $(v_2^1 - v_2^*)$ negative. Although liquids are more compressible than the corresponding solids the difference in compressibility does not produce a change of sign in the volume change on melting even at very high pressures. Simon,¹³ who proposed a semi-theoretical equation which represents the pressure-temperature relation along the melting curve of a pure solid sufficiently well in known cases to justify its use in extrapolation, concludes that even at very high pressures $(v_2^1 - v_2^*)$ never becomes zero and *a fortiori* never negative.

THE VOLUME CHANGES ON MIXING OF LIQUIDS

The quantity $(v_2 - v_2^1)$ represents the increase in volume which occurs when one gram of pure liquid solute mixes with a large amount of the saturated solution. In an ideal solu-

¹⁰ See J. Johnston: J. Geol., 23, 740, 1915.

¹¹ Cohen, E., and Moesveld, A. L. Th.: Z. phys. Chem., 93, 385, 1919.

¹² See Bridgman, P. W.: Proc. Nat. Acad. Sci., 23, 204, 1937.

¹³ Simon, F.: Trans. Faraday Soc., 33, 65, 1937.

tion as usually defined,¹⁴ $(v_2 - v_2^1)$ is zero. In such a solution the potential energy of a molecule due to its neighbors is approximately the same in the solution as in its own pure liquid. In such a case $(v_2^1 - v_2^s)$ is the predominating term and dx_2/dP is negative.¹⁵ Examples are known especially in mixtures of organic liquids where $(v_2 - v_2^1)$ is positive and hence dx_2/dP is decidedly negative. It is of interest to note that in these liquid mixtures considerable progress has been made in calculating the volume change on mixing from the free energy changes and hence approximately from the heats of evaporation of the pure liquids,¹⁶ showing a quantitative relationship between the cohesive forces in the pure components and the volume change on mixing.

In the majority of cases, however, especially where the solutes are solid at the temperature of the solution, a contraction occurs when the liquefied solute and the solvent mix, and if $(v_2 - v_2^1)$ is negative and larger than $(v_2^1 - v_2^s)$ the solubility of the solid will be raised by pressure, as in the cases of potassium sulphate or sodium chloride in water. It will be seen, therefore, that in general a solid is less soluble in a given liquid solution under high pressures than under low pressure, the only exceptional cases being those where the pure solid contracts on melting or where the volume change on mixing is negative and abnormally large.

TYPES OF COHESIVE FORCES AND THEIR INFLUENCE ON COMPRESSIBILITY AND VOLUME CHANGES.

When a given amount of one liquid dissolves in a solution the contraction in volume is proportional to the compressibility of the solution and to the magnitude of the intermolecular attractive forces between the solvent and the solute, modified by possible changes in the structure of the solution. It is

¹⁴ Hildebrand, J. H.: *Solubility of Non Electrolytes*, Reinhold Publishing Corporation, New York, p. 59, 1936.

¹⁵ For an ideal solution the change in solubility with pressure is given by the well-known formula

$$\frac{d \ln X_2}{dP} = - \frac{\Delta V}{RT}$$

where X_2 is the mol fraction of solute in the saturated solution, ΔV is the volume change per mole when the solute melts, and R is the ordinary gas constant.

¹⁶ Scatchard, G.: *Trans. Faraday Soc.*, 33, 160, 1937.

generally assumed that the intermolecular forces which hold the various units (molecules or ions) together in solids also account for the cohesion of liquids whether pure or mixed. The nature of these cohesive forces is now understood,¹⁷ and for convenience we may classify them as follows.

A. Non-directed Forces. (1) (a) Coulomb forces between charged ions. e.g. Forces in ionic crystals or liquids like NaCl. (b) Ion dipole forces. e.g. NaCl-H₂O solutions or electrolytes in general. The forces in group A (1) are strong and act over relatively long ranges. (2) Van der Waals' forces—under which heading come (a) The forces between permanent dipoles and between permanent and induced dipoles. (b) Dispersions forces; these are always present and predominate in organic liquids and solids. Dispersion forces account for the liquid and solid rare gases. (3) Repulsive forces.

B. Directed Forces. (1) Partially directed forces of the hydrogen or hydroxyl bond type¹⁸ as in water, ammonia, organic compounds containing oxygen and nitrogen, alcohols, amines, sugars. (2) *Covalent or homopolar* bond type of forces as in SiO₂, B₂O₃, silicates, phosphates, plastics, diamond. These forces are very strong and may range from a highly polarized electrostatic bond (A1) to the type of forces which hold the oxygen atoms together in a molecule. In addition to these, we have the cohesive forces in metals which fall in a different category.¹⁹

A knowledge of the chemical nature of a liquid or solid and structural information as given by X-ray diffraction patterns enables one to say what types of cohesive forces act in the liquid, but quantitative information about their macro-

¹⁷ Lennard-Jones, J. E.: Proc. Phys. Soc. London, 43, 461, 1931; Seitz, F., and Johnston, R. P.: J. Applied Phys., 8, 84, 186, 246, 1937; Herzfeld, K. F.: *ibid.*, 8, 319, 1937. London, F. (Trans. Faraday Soc., 33, 65, 1937) gives a clear account of van der Waals' forces. Hildebrand, J. H. (*ibid.*, p. 145), summarizes the types of forces encountered in solutions. Ewell, R. H. (J. Applied Phys., 9, 252, 1938), classifies the various types of forces in liquids in their relation to viscosity.

¹⁸ See Bernal, J. D., and Megaw, H. D.: Proc. Roy. Soc. A151, 384, 1935. For summary of recent literature see Ann. Reports Chem. Soc. Lond., 34, 89, 1937.

The term hydrogen bond is still vaguely used and in this paper it may be interpreted as meaning an electrostatic directed bond between residual charges associated with definite groups or atoms in different molecules.

¹⁹ See Mott, N. F., and Jones, H.: Theory of the Properties of Metals and Alloys, Clarendon Press, Oxford, 1936; also Mott, N. F.: Science Progress, 414, 1937.

scopic effects is obtainable only in simple cases. Much work has been done in relating heats of sublimation and evaporation, the melting points, the viscosity, the compressibility, etc. to the type and magnitude of the intermolecular forces.²⁰

Concerning the compressibility, we may make the following approximate statement about substances in the vicinity of their melting temperatures. In non-polar compounds (e.g. hydrocarbons, benzene, etc.) where only dispersion forces act, the compressibility is large; introduction of polar groups (e.g. chlorobenzene) to give permanent dipoles lowers the compressibility, hydrogen or hydroxyl bonds produce a still greater diminution, ionic forces still more, and the covalent bond type of cohesive forces produces the lowest compressibilities in liquids or solids. It should be mentioned that directed forces in a liquid may produce structural effects which complicate these simple conclusions. These will be dealt with later.

Empirically it has been found that the internal pressure set up by these cohesive forces is a useful quantity in a semi-quantitative treatment of liquids and solutions under pressure, and a consideration of this internal pressure leads to a formula which gives a clear picture of the factors determining ($v_2-v_2^1$) in certain types of solutions.

INTERNAL PRESSURE AND THE COMPRESSIBILITY OF LIQUIDS AND SOLIDS.

The compressions of a wide variety of liquids may be represented quite accurately by the Tait equation

$$-\Delta_P v = C \ln \frac{B + P}{B} \quad (2)$$

which in all cases holds best at the higher pressures. ($-\Delta_P v$ represents the change in specific volume when the pressure changes from zero to P , and C and B are positive constants.) By studying the compressions of benzene²¹ at different temperatures we have found that B may be taken as a measure of the difference between the expansive pressure due to the thermal energy of the molecules and the cohesive pressure due to the

²⁰ See, for example, the tables given by A. G. Ward, *Trans. Faraday Soc.*, 33, 91, 1937; also T. W. Richards, *Chem. Rev.*, 2, 331, 1925.

²¹ Gibson, R. E., and Kincaid, J. F.: *J. Am. Chem. Soc.*, 60, 511, 1938.

temperature-independent attractive forces between the molecules, and it seems safe to extend this conclusion qualitatively to other liquids.²² The quantity B , therefore, measures the net cohesive pressure, decreasing as the temperature is raised and increasing as the intermolecular attractive forces increase, and it may be determined directly from compressions at different pressures. In Table II we give values of the constants in the Tait equation for some substances at 25°.

TABLE II.

Values of the constants B and C' in the Tait equations for different substances.

$$-\frac{\Delta V}{V(P=0)} = C' \log \frac{B + P}{B}$$

Substance and temperature	C'	B (in bars)
Benzene (25°)	0.2159	970
Benzene (65°)	0.2159	701
Aniline (25°)	0.2159	2009
Aniline (65°)	0.2159	1606
Methanol (25°)	0.2208	764
Glycol (25°)	0.2280	2706
Water (25°)	0.3150	2996
Water (65°)	0.3150	3053
Sodium chloride (25°)	0.5013	51970

INTERNAL PRESSURES OF SOLUTIONS.

The internal pressures in pure liquids are set up by cohesive forces between like molecules, and these generally involve only one or two of the types of cohesive forces mentioned above. In solutions, however, the picture is complicated. The potential fields around the solvent and solute molecules are in general different not only in magnitude, but also they may arise from different types of forces.²³ Thus, as we vary the proportions of the components, we may expect significant changes in the

²² For theoretical discussions of equations of state similar in form to the Tait equation see Kincaid, J. F., and Eyring, H.: *J. Chem. Phys.* 5, 587, 1937; and Hudleston, L. J.: *Trans. Faraday Soc.*, 33, 98, 1937.

²³ It should be noted that we do not mean fundamentally different types of forces as all arise from electronic distributions, but only different types in the classification given above, a classification which is now widely used for the sake of convenience.

internal pressures of solutions, and it is found that this change of internal pressure with concentration is a useful quantity to consider and may be related to the compressibilities of the pure components.

If we have two molecular species, X representing the solvent and Y the solute, mixing to form a solution, it is clear that the mutual potential energy of molecules X and Y must be approximately the same or greater than the mutual potential energies of the molecules X and X or Y and Y . Thus with solutes possessing high internal pressures (large Y — Y forces) and hence low compressibilities in the pure solid or liquid state, we should expect large X — Y forces and hence a large volume change on mixing, especially if the X — X forces are small. It is convenient, therefore, to divide solutions into two classes: (a) those in which the compressibilities of the pure components are close together, and (b) those in which the compressibilities of the pure components are widely different.

In solutions of type (a) the solubility of the solid solute will decrease with pressure (provided the solid expands on melting), even at low pressures and we need discuss this no further at present. On the other hand, in solutions of type (b) increase in solubility with pressure will occur under certain conditions, and, as this represents an important class of solutions, we shall discuss it further, particularly as solutions of this class are well adapted to a quantitative treatment.

Application of the hypothesis of Tammann²⁴ that the solvent in a solution behaves as the pure solvent under a given external pressure P_0 leads to an equation for the compressions of solutions which we have found empirically to be valid over wide pressure ranges,²⁵ the quantity P_0 being computed from the compression at one pressure. According to this hypothesis the apparent volume of the solvent in the solution, ϕ_1 , computed on the assumption²⁶ that the specific volume of the solute in the solution is v_2^1 is given by

$$\phi_1 = v_w - C \ln \frac{B + P_0 + P}{B + P} \quad (3)$$

²⁴ Tammann, G.: Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen, Leipzig, p. 36, 1907.

²⁵ Gibson, R. E.: J. Am. Chem. Soc., 56, 865, 1934.

²⁶ A justifiable assumption if the compressibility of the solute is much less than that of the solvent.

Now it may readily be shown²⁷ that

$$(v_2 - v_2^1) = -x_1^2 \frac{d\phi_1}{dx_1} \quad (4)$$

On combining equations (3) and (4) we obtain

$$(v_2 - v_2^1) = x_1^2 \frac{C}{B + P_s + P} \frac{d(B + P_s)}{dx_1} \quad (5)$$

or, as it is very convenient in comparing solutions with the same solvent but different solutes to use as the concentration unit the number of gram molecules of solute per 1000 grams of solvent and to use the molal volumes V_2 and V_2^1 of the solute, we may make the transformation and obtain the desired equation (6):

$$(V_2 - V_2^1) = -\frac{1000 C}{B + P_s + P} \frac{d(B + P_s)}{dm} \quad (6)$$

This equation, which is empirical, seems to be valid at any pressure and it should be noted that B , C , and P_s are all independent of pressure. It must be admitted, however, that the equation is approximate. In the calculation of P_s from compressibility data some assumption must be made about the contribution of the solute to the compressibility of the solution and this assumption is rather important in determining the slope of the $(B + P_s)$ —concentration curves at high concentrations. Little is known about the difference between the compressibilities of solids and liquids²⁸ and we have generally assumed that the compressibility of the solute in the solution is the same as that of the solid solute. Comparison of $(V_2 - V_2^1)$ as

²⁷ If x_1 and x_2 are the weight fractions of solvent and solute respectively, if v is the specific volume of the solution and v_1 and v_2 are the partial volumes of the solvent and solute, then by definition

$$v = x_1 v_1 + x_2 v_2$$

$$v = x_1 \phi_1 + x_2 v_2^1$$

whence $(v_2 - v_2^1) = \frac{x_1}{x_2} (\phi_1 - v_1)$.

But $v_1 = x_1 x_2 \frac{d\phi_1}{dx_1} + \phi_1$, whence equation (4) follows.

²⁸ Richards, T. W., and Speyers, C. (J. Am. Chem. Soc., 36, 494, 1914) found that liquid water was about four times as compressible as ice at approximately the same temperature, and Richards, Bartlett, and Hodges (J. Am. Chem. Soc., 43, 1538, 1921) found that melting doubled the compressibility of benzene.

computed from equation (6) with directly observed values of V_2 shows that V_2^1 diminishes slightly with concentration, whereas it should be constant. If one assumes that the compressibility of the solute is three times as great in the solution

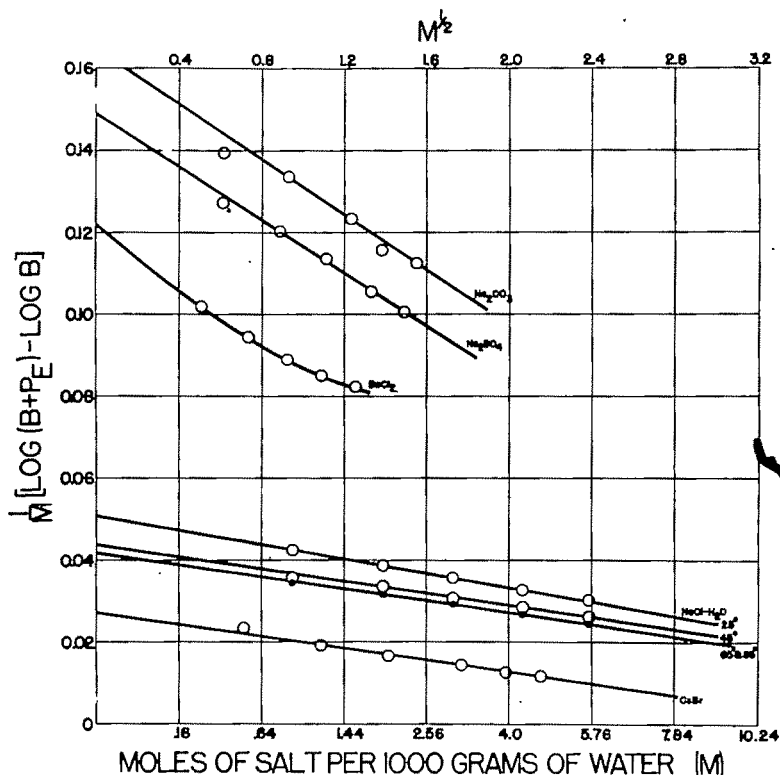


Fig. 2. Curves showing the relationship between $(\log(B + P_e) - \log B)/m$ and the square root of the molal concentration for different salts. The ordinate is determined from compressibility measurements and is directly related to the volume change on mixing of the liquid solvent and solute. In cases where V_2 varies approximately linearly with $m^{1/2}$ the same relation holds for $(\log(B + P_e) - \log B)/m$ vs. $m^{1/2}$. Neither curve is linear in the case of $\text{BaCl}_2\text{-H}_2\text{O}$ solutions.

as in the solid state, the values of V_2^1 obtained are quite independent of concentration. On the other hand, it has been shown by a number of investigators²⁹ that V_2 is a linear func-

²⁹ The literature is extensive. A good résumé is given by F. T. Gucker, J. Phys. Chem., 38, 307, 1934.

tion of the square root of the concentration for electrolytic solutions, and hence if equation (6) is valid, the expression $(\log (B + P_s) - \log B)/m$ should also be a linear function of the square root of the concentration. The curves in Fig. 2 show that this is the case. If the lines in this figure are expressed by the equation

$$(\log (B + P_s) - \log B)/m = a + \beta m^{1/2}$$

it follows from equation (6) that $(V_2 - V_2^1) = -2303 C (a + \frac{3}{2} \beta m^{1/2})$. Equation (6) is interesting from two points of view; in the first place it enables one to calculate approximate values of the volume change on mixing from compressibilities alone, and in the second place it summarizes concisely the factors which determine the sign and magnitude of $(V_2 - V_2^1)$.

The term $\frac{1000 C}{B + P_s + P}$ represents the compressibility per

1000 grams of the solvent³⁰ at an external pressure $(P_s + P)$. By Tammann's hypothesis it is the compressibility of the solvent in the solution at pressure P . We thus see the rôle played by the compressibility of the solvent in determining the volume change on mixing, a feature which has not been sufficiently emphasized in the past.

The second half of the right-hand side of equation (6) represents the change in the net internal pressure of the solution per gram molecule of solute added, and is related to the compressibility of the pure solute. In solutes with high internal pressures, and hence low compressibilities in the pure solid or liquid state, we have seen that large $X-Y$ forces and hence large values of $d(B + P_s)/dm$ when they dissolve in a solvent are to be expected. Equation (6) shows, therefore, that $(V_2 - V_2^1)$ will be large if the pure components differ widely in compressibility and that a knowledge of the compressibilities of the components gives some clue as to the effect of pressure on solubility. Furthermore, as P_s increases with the concentration of the solute, and as equation (6) indicates that $(V_2 - V_2^1)$ varies inversely as P_s , it follows that the more soluble a solid is at atmospheric pressure, the less chance there

³⁰ This follows if equation (2) be differentiated with respect to pressure and it is noted that $\frac{dv_s}{dP} = -\frac{C}{B + P}$, where v_s is the specific volume of the pure solvent.

is that its solubility will increase with pressure. The inverse proportionality between $(V_2 - V_2^1)$ and the external pressure P also indicates that at sufficiently high pressures $(V_2 - V_2^1)$ will become so close to zero that the pressure coefficient of the solubility will be negative for all normally melting solids. Likewise if the pure solvent has a low compressibility, B itself will be large and $(V_2 - V_2^1)$ be correspondingly reduced in magnitude. To sum up, we may say equation (6) shows that a high concentration of solute, high external pressure, low compressibility of the solvent, and low change of internal pressure with concentration all tend to prevent the solubility of a solid from increasing with pressure.

AQUEOUS SOLUTIONS.

Compared with other substances which are liquid at the same temperature, water has a low compressibility and the cohesive forces are large, being of the types A2 and B1.³¹ Water is, however, between five and ten times as compressible as many of the solids which dissolve freely in it. These solids are of two main classes: (1) organic compounds containing oxygen, especially OH groups or nitrogen such as alcohols, sugars, amides, etc., in which forces of type B1 prevail; and (2) inorganic compounds in which the main cohesive forces are of type A1 together with van der Waals' forces. In the soluble inorganic substances the ionic forces account for most of the cohesive energy of the solids as in the alkali halides, whereas in the insoluble salts the van der Waals' forces contribute significantly to the cohesive energy as in silver or cuprous chlorides.³² In organic compounds containing many hydroxyl groups, the internal pressures may become very large as in the sugars, and when these dissolve in water a very significant contraction occurs, or, in other words, $d(B + P_0)/dm$ is large. For example, the solubility of mannitol increases initially with pressure.³³ In solutions of inorganic substances in water very large cohesive forces prevail owing to the interaction of their ions on the water dipoles, and these forces increase with the charge on the ions and diminish as their radii

³¹ Bernal, J. D., and Fowler, R. H.: *J. Chem. Phys.*, 1, 540, 1933.

³² Mayer, J. E.: *J. Chem. Phys.*, 1, 327, 1933.

³³ Cohen, E., Inouye, K., and Euwen, C.: *Z. phys. Chem.*, 75, 257, 1911.

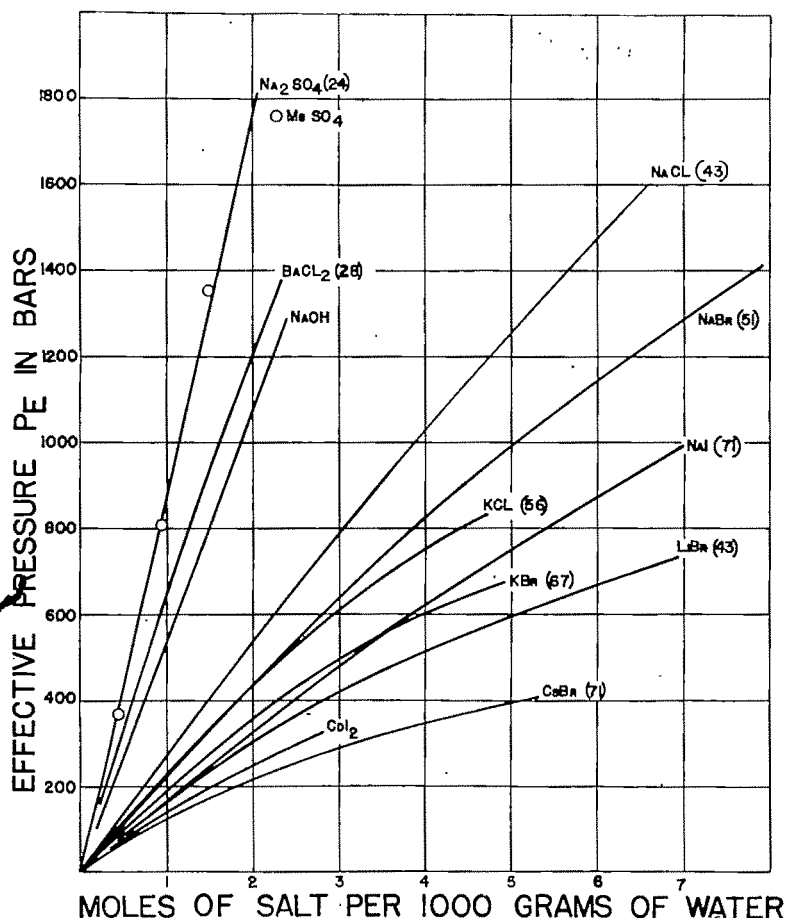


Fig. 3. Illustration of the dependence of the slope, $\frac{d(B+P_*)}{dm}$, on the nature of the solute for aqueous solutions. The figures in parenthesis give the compressibilities of the solid solutes at atmospheric pressure in reciprocal bars $\times 10^{-7}$. The parallelism between the slopes of the curves and the compressibility of the solute will be noted. Exceptions are illustrated by LiBr and CsBr solutions. In the latter case a change in solid structure gives rise to a lower compressibility of the solid than would be expected from a consideration of other alkali bromides.

increase. A glance at Fig. 3 will show the effects of these two factors, which have been discussed more fully elsewhere.⁸⁴

⁸⁴ Gibson, R. E.: Sci. Monthly, 46, 103, 1938.

P_0 rises most sharply with concentration in solutions containing the most highly charged ions, and especially in solutions of sulphates and carbonates (bivalent anions). In solutions of hydroxyl ions the greatest values of $d(B + P_0)/dm$ for monovalent ions are found. It will be noticed that $d(B + P_0)/dm$ increases as the compressibility of the solute decreases, and in this connection it is of interest to note an empirical relation between the compressibility β , the molal volume V , and the valency Z in ionic crystals, viz. $\beta = V/Z \times 5.6 \times 10^{12}$ given by Balce.³⁵

These considerations lead to one definite conclusion of direct geochemical interest. Saturated solutions of sparingly soluble salts such as the sulphates, fluorides, carbonates, or the sulphides of the alkaline earths, the rare earths and the heavy metals, the metallic oxides or hydroxides, are examples of the one case where we may definitely say that pressure will increase their solubility. Chemically and physically they give solutions of the potassium sulphate—water type. Referring to equation (6) we may say that $d(B + P_0)/dm$ is large, $(B + P)$ is small, and as the solutions are very dilute, P_0 is also small—the conditions are right for $(V_2 - V_2^s)$ being large and negative.

In order to estimate roughly the magnitude of the increase with pressure of the solubility of sparingly soluble substances, we may throw equation (1) into the following form.³⁶

$$\frac{dm}{dP} = - \frac{(V_2 - V_2^s)m}{vRT \left(1 + m \frac{\partial \ln \gamma}{\partial m} \right)} \quad (7)$$

The quantity $\partial \ln \gamma / \partial m$ is always negative in dilute solutions of electrolytes,³⁷ and if m is small we may take RT as the upper limit of the denominator and notice that neglect of $m \partial \ln \gamma / \partial m$ gives us the lower limit of dm/dP .

Data from which we might calculate V_2 in saturated solutions of sparingly soluble substances are practically nonexistent, but it is possible to arrive at fair estimates from values of v_2 for the corresponding types of salts at low concentrations obtainable from curves such as are given in Fig. 1. The results of a

³⁵ Balce, S.: Philippine J. Sci., 60, 251, 1936.

³⁶ In this equation γ is the activity coefficient of the solute as usually defined (see Adams, L. H.: Chem. Rev., 19, 1, 1936). v is the number of ions into which the electrolyte dissociates.

³⁷ See Harned, H. S.: Taylor's Treatise on Physical Chemistry, 2d ed., p. 773. Van Nostrand Co., New York, 1930.

few approximate calculations of dm/dP for different insoluble substances are given in Table III. They show quite clearly

TABLE III.

Rough estimates of the percentage change in the solubility of sparingly soluble substances in water produced by an increase of pressure from 1 to 1,000 bars.

Substance	Solubility moles per 1000 grams water	V_2^s (ml/mole)	V_2 (ml/mole)	vRT ml \times kilobars	Percentage increase in solubility per 1000 bars increase in pressure
CaCO ₃	0.00057	36.9	<0	49.5	75
Ca(OH) ₂	.022	33.1	<0	74.3	44
CaSO ₄ (anhydrite)	.0046	47.8	10	49.5	77
CaSO ₄ ·2H ₂ O	.0153	74.0	46	49.5	57
CaF ₂	.00021	24.5	0	74.3	33
CaS	.028	28.2	0	49.5	57

that even a pressure increase of 1000 bars (corresponding to the pressure in the depths of the ocean) will increase the solubility of sparingly soluble electrolytes in water between 10 and 50 per cent of its value at atmospheric pressure. Movement of water from deeper to shallower parts of the ocean may account, therefore, for considerable transport and reprecipitation of solids if saturation conditions are approached. Experimental work to determine the effect of pressure on the solubility of interesting sparingly soluble substances in water is being started, and further discussion of its implications must await quantitative results.

THE EFFECT OF TEMPERATURE.

Normally, rise of temperature increases the compressibility of solids and liquids and thus we should expect $(v_2 - v_2^s)$ to become more negative as the temperature is raised; in other words the partial thermal expansion of the solute should be negative. This is the case in many solutions where contraction occurs on mixing, e.g. sodium iodide in glycol, sodium iodide in methanol.⁸⁸ Water, however, is exceptional in that its compressibility falls off as the temperature rises, passing through a minimum near 50°. In aqueous solutions below about 65° v_2 increases rapidly with temperature and $(v_2 - v_2^s)$ gets closer to zero. Thus in aqueous solutions where the solubility

⁸⁸ Gibson, R. E., and Kincaid, J. F.: J. Am. Chem. Soc., 59, 579, 1937.

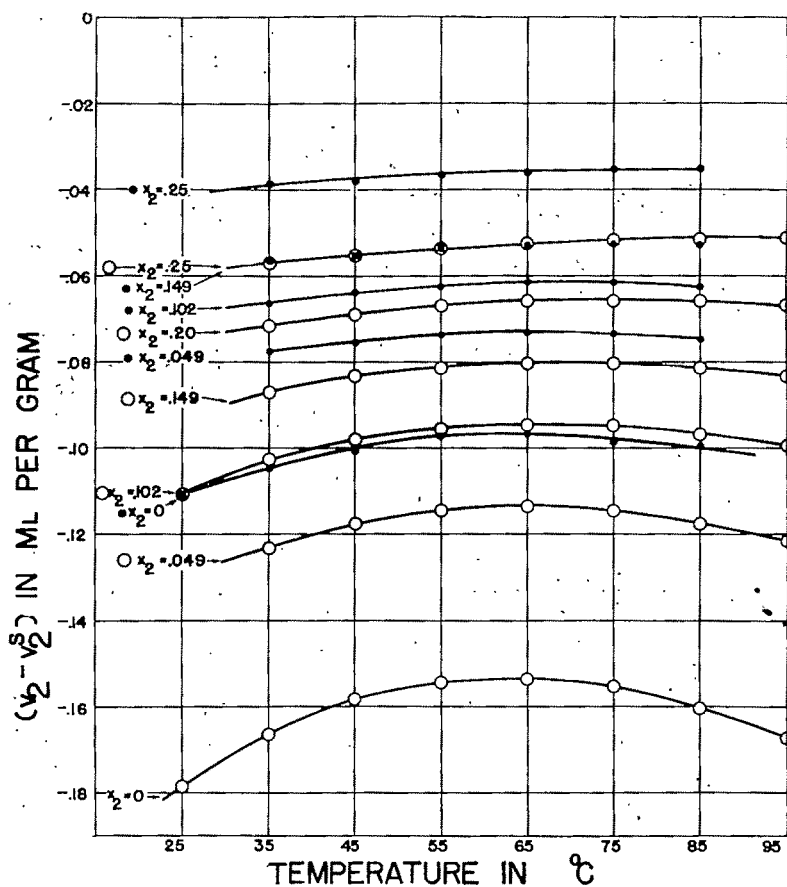


Fig. 4. The expansions per gram when sodium chloride dissolves in solutions of different concentration at different temperatures and pressures.

The open circles O refer to atmospheric pressure and the dots ● refer to measurements at 1000 bars.

It will be noted that the expansions pass through maxima as the temperature is raised and that increase of pressure and of concentration flattens the curves and makes the values of $(v_2 - v_2^0)$ less negative.

increases with pressure, increase of temperature will lower $\frac{dm}{dP}$. However, above 65° the partial volumes of electrolytes dissolved in water go through a maximum and begin to diminish as temperature continues to rise.⁸⁹ With Mr. O. H.

⁸⁹ Bousfield, W. R., and Lowry, T. M.: *Trans. Faraday Soc.*, 6, 15, 1910; Pesce, B.: *Gazz. chim. ital.*, 66, 99, 1936; Akerlof, G., and Teare, J.: *J. Am. Chem. Soc.*, 60, 1226, 1938.

Loeffler⁴⁰ we have recently obtained data for sodium chloride, sodium bromide, and lithium bromide solutions up to 95° and a sample of the results is shown in Fig. 4. It will be seen that the maximum occurs at lower temperatures in the dilute than in the concentrated solutions. In 5.5 and 45:1 per cent lithium bromide solutions the maxima are at 45 and 55° respectively.

Bousfield and Lowry showed that the apparent volumes of lithium and calcium chlorides and alkali hydroxides in water passed through maxima at still lower temperatures and thereafter decreased very rapidly. The curves given in Fig. 4 are, therefore, typical and we may conclude that at temperatures above 60° the effect of pressure in increasing the solubility of the sparingly soluble salts we have discussed will be enhanced by rise of temperature, and there is no reason to suppose that this conclusion needs to be modified at the critical temperature.

We have mentioned that in liquid water partially directed forces of the hydrogen or hydroxyl bond type exist among the molecules and this produces a type of structure in the liquid.³¹ In the effect of temperature and addition of solutes on this liquid structure lies the explanation of the curious partial volume-temperature curves we have discussed—this will be set forward elsewhere. It is to be emphasized, however, that the liquid structures set up by the directed forces among the molecules do cause considerable modification of the conclusions we have just given. For example, although the forces between lithium ions and water molecules are very large, $(V_2 - V_2^*)$ is actually positive in concentrated solutions of several lithium salts, whereas the comparative compressibilities of these salts and water would lead one to expect it to be large and negative. Furthermore, in glycol, which is only three quarters as compressible as water, $(V_2 - V_2^*)$ for lithium bromide is much less than in water solutions. These apparent anomalies have been explained elsewhere on the basis of the arrangement of the molecules in water.⁴¹

COMPOUNDS AS SOLID PHASES.

Frequently the solid phase in equilibrium with a solution is a compound of both end members of the system, hydrates such as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ being typical examples. Such solids are always more compressible than the solute end-member and the

⁴⁰ Gibson, R. E., and Loeffler, O. H.: Unpublished results of work at the Geophysical Laboratory.

⁴¹ Gibson, R. E., and Kincaid, J. F.: *J. Am. Chem. Soc.*, 59, 579, 1937.

foregoing discussion leads to the conclusion that their solubilities will be raised by pressure much less than those of the end members. The partial molal volume V_{XY} of a compound whose formula is $mXnY$ is given by $V_{XY} = mV_X + nV_Y$ where V_X and V_Y are the partial molal volumes of the solvent X and the end member Y in the solution. Using this formula, together with the densities of the solid hydrates given in the literature, we obtained $(v_2 - v_2^*)$ for the hydrates $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{NaBr} \cdot 2\text{H}_2\text{O}$. These are plotted against the concentration in Fig. 1. In both cases $(v_2 - v_2^*)$ is less negative than for the corresponding pure salt and, indeed, it will be seen that for $\text{NaBr} \cdot 2\text{H}_2\text{O}$ it is actually positive in the concentrated solutions. Thus while the solubility of NaBr in water, like that of NaCl , is initially raised by pressure, the solubility of $\text{NaBr} \cdot 2\text{H}_2\text{O}$ is always diminished by pressure, and direct experiments made in this Laboratory have shown that this diminution is considerable.

THE EFFECT OF PRESSURE ON THE SOLUBILITY OF MINERALS IN SILICATE MELTS.

In applying the foregoing discussion to a consideration of the effect of pressure on the solubility of solid silicate minerals in silicate melts we may note at once that the intermolecular forces are large both in the solvent and the solute, that the compressibilities are very low, and that the solutions and the solid phases are chemically similar. These systems are of type (a) in which the compressibilities of both components are close together and also share the characteristics we have mentioned in the previous section on compound formation. We may therefore state with some confidence that these considerations all make it improbable that increase of pressure will increase the solubilities of these solids, and that they really favor the opposite conclusion.

The data given by Day and Allen⁴² on the densities of albite-anorthite glasses and solid solutions indicate no appreciable volume change on mixing and thus the volume changes on melting of the end members govern the effect of pressure on the solidus and liquidus curves in this system. Bowen,⁴³ indeed, has shown that the solutions in this system conform very closely

⁴² Day, A. L., and Allen, E. T.: *The Isomorphism and Thermal Properties of the Feldspars*, Carnegie Inst. Wash. Pub. No. 31, 74, 1905.

⁴³ Bowen, N. L.: *This Journal*, 35, 577, 1913.

to ideal behavior. From the data on the densities of soda-silica glasses⁴⁴ one may compute the partial volumes of SiO_2 dissolved in Na_2SiO_3 , at room temperature. The partial volumes of SiO_2 in solutions from 60 to 100 per cent SiO_2 are greater than the specific volume of tridymite at the same temperature. In view of the interval between room temperature and the temperature at which tridymite and soda-silica melts are in equilibrium, we cannot attach much weight to this observation. Qualitatively it is compatible with the foregoing discussion.

We have noted that the cohesive forces in silicate solids and liquids are of the covalent bond type, strong and directed forces which produce a quasi structure in the liquids, accounting among other phenomena for the high viscosity of melted silicates.⁴⁵ The structural or association effects in silicate liquids introduce complications which make further speculations very risky. Suffice it to say that influences of the structural effects in the liquids both on the volume change on melting and on the volume changes on mixing when components of different valencies and coordination numbers are introduced must be expected and investigated before further progress is made.

⁴⁴ Morey, G. W., and Merwin, H. E.: *J. Optical Soc. Am.*, 22, 632, 1932.

⁴⁵ Ewell, R. H.: *op. cit.*

SILICATE—WATER SYSTEMS: PHASE EQUILIBRIA IN THE $\text{NaAlSi}_3\text{O}_8$ — H_2O AND KAlSi_3O_8 — H_2O SYSTEMS AT HIGH TEMPERATURES AND PRESSURES.

ROY W. GORANSON.

ABSTRACT.

The subject matter herein includes experimentally determined phase equilibria relations for the albite—water and orthoclase—water systems from 800 to 1200° C. and pressures to 4000 bars and is a part of the series constituting a program of research on silicate—water systems begun some years ago by the writer.

The freezing-point curves of these systems extend out into three-dimensional temperature-pressure-concentration space and have been completed for albite—water. The orthoclase—water system is somewhat more complex in that at low pressures, i.e. to about 2600 bars, orthoclase melts incongruently to leucite and liquid. The solubility of water in this liquid has not yet been completely determined as a function of temperature and pressure so that only the projection of the freezing-point curve on the temperature-pressure coordinate plane is given herein for the latter system.

In order to obtain other thermodynamic data such as apparent volumes and heats of evaporation it was necessary to obtain the temperature-pressure-volume relations of water in this region. These latter data are in large part extrapolated, consequently the derived thermodynamic quantities will have a lower degree of accuracy.

The data show that the pressures developed on crystallization may not only comply with but actually exceed the pressures necessary to explain certain volcanic phenomena.

INTRODUCTION.

In this paper are presented phase equilibria relations for the systems, $\text{NaAlSi}_3\text{O}_8$ — H_2O and KAlSi_3O_8 — H_2O , in the temperature range from 800° C. to 1200° C. and pressures to 4000 bars (metric atmospheres). In the course of these studies many improvements and plans for future improvement were evolved which will increase the accuracy of further studies on these systems. It is hoped, however, that the present report will be of interest not only because this combined temperature and pressure range is unique, but also because these systems represent the first laboratory investigation of truly rock-forming silicates which include water as a component.

In order to correlate the results of these studies and apply them to the understanding of other silicate-water systems it is necessary to know not only the heterogeneous equilibria relations but also the properties of each of the coexistent

homogeneous parts or phases. In these investigations the homogeneous parts are: (1) a vapor phase which is essentially water, (2) a liquid phase which is a saturated solution of water in silicate melt, and (3) solid phase or phases consisting of one or more silicates. As progress in this direction there is presented, in addition to the vapor-liquidus-solidus curves of these systems, (a) an equation of state for water in this temperature and pressure range, (b) experimentally determined solubility relations of water in silicate melts as functions of temperature and pressure, and (c) derivations of the necessary correlative thermodynamic equations together with such interpretations as could be made from these data.

APPARATUS AND TECHNIQUE.

The high pressure furnace or bomb in which the runs were made is a modification of the apparatus described elsewhere¹ and will be discussed in detail in a forthcoming paper.

The charges, consisting of very finely-ground powder of the silicate under investigation and water, are sealed gas-tight in platinum capsules. The water content is adjusted so that the minimum amount in excess of that necessary to saturate the silicate solution will be present. Fine grinding of the silicate is necessary to prevent puncture of the capsule and also to lessen the time necessary for attainment of equilibrium. The operation of sealing the capsules gas-tight is essential for several reasons, the most important one being to insure that a closed system is obtained.

If water could circulate freely in the bomb the vapor phase would be non-uniform as to temperature, and consequently leaching and deposition cycles would take place with a resulting change in composition of the silicate—presumably an eventual steady state might be attained for these particular conditions but it would not be the one desired.

For a particular run two or more of these capsules are inserted in the pressure furnace in close proximity to the two thermocouples, one of which is near the top end and the other near the bottom end of the capsules. The pressure medium is nitrogen and is compressed by a hydraulic piston which is operated from a hydraulic compressor. The compressed gas in the bomb acts only on the exterior of the platinum capsules.

¹ Goranson, R. W.: This Journal, 22, 481-502, 1931.

The pressure is determined by measuring resistance changes under pressure of a 100 ohm. coil of manganin wire calibrated by comparison with a free-piston type gauge. The sensitivity of this pressure measuring device is about a tenth of a bar (a change of about 0.2 ohm. per kilobar) and is reproducible to within a bar. The temperature is then raised by applying electrical power to three electrodes which enter the bomb through gas-tight electrically-insulating packings and connect to a platinum-rhodium resistance furnace inside the bomb. The temperature is determined by measuring the electromotive force of two platinum—platinum rhodium thermocouples which enter the bomb through specially devised gas-tight electrically-insulating packings. They are calibrated by means of suitable fixed points such as the melting temperature of pure gold.

The silicate glasses were prepared synthetically to insure their purity and for them the writer is indebted to Dr. J. F. Schairer of this Laboratory.

For a particular run pressure and then temperature are raised to the desired amounts and held at these values for a length of time sufficient for attainment of equilibrium. Although these silicates are very sluggish in crystallizing from an anhydrous melt they crystallize very readily from hydrous solutions, in fact relatively large crystals have been grown in half an hour. At the end of the run the electric power supply is cut off, the temperature dropping rapidly enough to freeze the equilibrium, i.e. the charges are quenched. Finally the pressure is released. The capsules are then cut open and examined under the microscope for changes in state and if no crystallization has occurred the glasses are analyzed for water content. To do this the excess water in the capsule is evaporated off, the glass weighed on a micro balance, ignited, and then weighed again.

THERMODYNAMIC PROPERTIES OF WATER FOR TEMPERATURES
BETWEEN 800 AND 1200° AND PRESSURES TO 4000 BARS.

Keenan and Keyes² have recently published superheated steam tables for temperatures to 875° C. and pressures to 380 bars. Van Nieuwenburg and Blumendal³ have measured the

² Keenan, J. H., and Keyes, F. G.: *Thermodynamic Properties of Steam*, John Wiley and Sons, New York, 1936.

³ Van Nieuwenburg, C. J., and Blumendal, H. B.: *Recueil des travaux chimiques des Pays-Bas*, 51, 707-714, 1932.

specific volumes between 350 and 480° C. at pressures from 160 to about 600 bars. Where overlapping occurs these two sets of data agree rather well. Tammann and Rührenbeck⁴ determined the specific volume of water between 20° and 650° C. at pressures to about 2500 bars. This third set of high-temperature data does not, however, agree with the above two nor with the few measurements made by the writer. Tammann and Rührenbeck's method required the use of a mercury piston and consequently corrections of uncertain magnitude. Therefore, although their data were not used as such herein, it was assumed that their slopes would be considerably more accurate than their absolute values and thus some of the derivatives computed from their data were utilized.

The determinations which have been made by the writer are in the nature of trial runs carried out to test the feasibility of the method devised. Varying proportions of water are sealed up in platinum capsules and inserted in the bomb as described under "Apparatus." Pressure developed in the bomb acts only on the exterior of the capsules and when the amount desired is attained the temperature is then slowly raised as for a heating-curve run. When the internal pressure exerted by the water exceeds the nitrogen pressure applied externally on the walls of the platinum envelope the capsule punctures at a point of weakness and this is indicated by a sudden drop in the thermocouple reading. The shape and stretch of the capsule at the time of rupture are retained, the perforation preventing collapse, and therefore the volume capacity of the tube may be ascertained after removal from the bomb. The corrections to be made are for the volume change of the platinum itself between room temperature and atmospheric pressure and the temperature-pressure conditions at the time of rupture. Since the amount of water inserted is known, by previous weighing, the specific volume of the water at the temperature and pressure of rupture is determinable.

The many attempts to obtain equations of state and accurate interpolation formulae for gases have resulted in expressions of increased complexity and with increasing number of disposable constants. For example, Becker's expression, which will represent Bridgman's⁵ data for nitrogen gas, has four disposable parameters and, since the data are for one tempera-

⁴ Tammann, G., and Rührenbeck, Ad.: *Ann. Physik*, 13, 63-79, 1932.

⁵ Bridgman, P. W.: *Proc. Am. Acad. Arts Sci.* 59, 209, 1924.

ture, these parameters may also be functions of temperature. However, owing to the inequalities and scattered nature of the data used here for water, the best expression for representation of this material is, paradoxical as it may first seem, one which contains few disposable parameters. Attempts were therefore made to fit two parameter equations such as the van der Waals and the Dieterici type.⁶ On solving for the parameter

$$a = v^2 \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right]$$

in the van der Waals expression it was found that the parameter b must be treated as a function of temperature and perhaps of volume. On the other hand after solving for the parameter

$$a = \frac{2}{3} RT^{3/2} \frac{v}{p} \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right]$$

it was found that the other parameter b of the Dieterici type had no noticeable trend and deviated by only 3% from the mean over the twenty-one points fitted.

The equation finally adopted to express the p - v - T relations for water at high temperatures is

$$p = \frac{4.619 T}{v - 1.9} \exp \frac{-1.08 \times 10^5}{v T^{3/2}} \quad (1)$$

where p is expressed in bars, v in $\text{cm}^3/\text{g.}$ and T in degrees Abs. A plot of $pv - 4.619T$ against pressure is given in Fig. 1.

Although no particular attempt was made to fit the equation to low pressure data it was found that the values of p as calculated by this equation were less by about 0.4 bars than the values as given by Keenan and Keyes for the 871°C. isotherm but without any trend.

Moreover according to this equation the Boyle point is at about 1200°C. , i.e. it reduces to $pv = RT$ for pressures less than 100 bars at 1200°C.

⁶ Van der Waals' equation (1873): $(p + \frac{a}{v^2})(v - b) = RT$

Dieterici's equation (1898): $p(v - b) = RTe^{-a/RTv}$
where a , b , and R are constants.

Now for an ideal gas we have

$$S(T, p) = S(T, 1) - \int_1^p R \, d \ln p$$

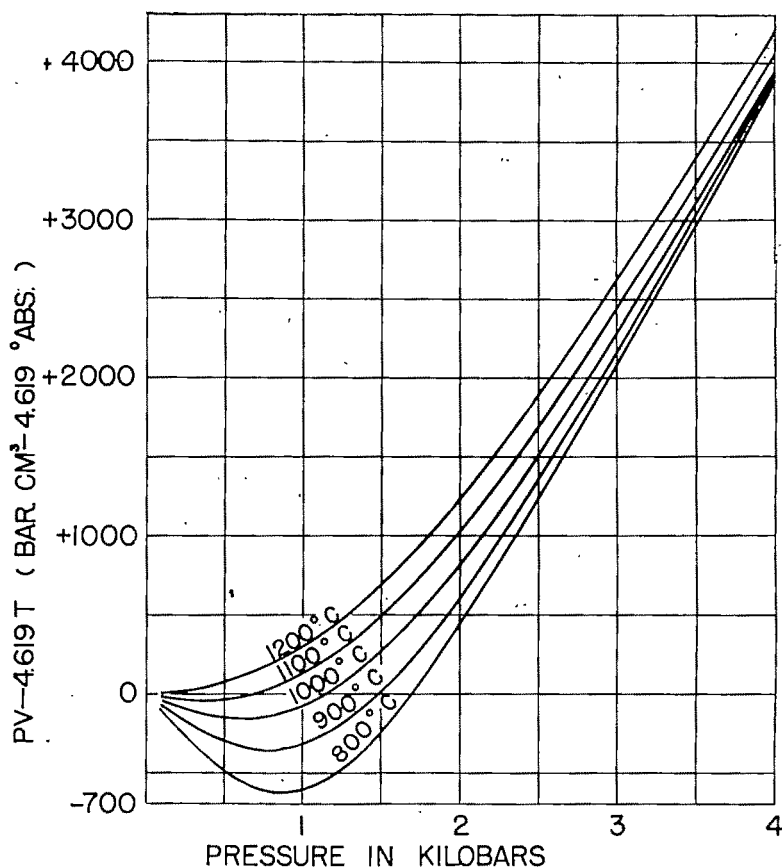


Fig. 1. p - v - T relations for water in the temperature range from 800 to 1200° C. Deviations from the perfect gas law, $p v - 4.619 T$, in terms of bar cm^3 are plotted as ordinates and pressures in kilobars as abscissae.

where $S(T, p)$ and $S(T, 1)$ denotes the entropies at the states (T, p) and $(T, p=1 \text{ bar})$ respectively; R denotes the gas constant. Thus $\partial^2 S / \partial T \partial p$ is zero, i.e. the change of entropy with temperature is the same for all pressures, and furthermore the change of enthalpy with pressure, $\partial H / \partial p$, is also zero. There-

fore, for pressures of 100 bars or less, the isopiestic enthalpy curves should all cross the 1200° C. isotherm at the same point and with the same slope, similarly the isopiestic entropy curves should all cross this isotherm with the same slope but separated by distances equal to $R \ln (p_1/p_2)$ where p_1 and p_2 are the pressures of two neighboring curves. A plot of enthalpy and entropy data from Gordon's⁷ spectroscopic measurements (1 atm. ideal gas) and from Keenan and Keyes' Tables² indicates that the isopiestic curves of

$$S(T, p) + \int_1^p R d \ln p$$

will extrapolate to meet at about 1200° and with the same slope, and that the enthalpy curves will do the same thing. The latter plot is not so diagnostic because of the greater curvature of the enthalpy diagrams.

SOLUBILITY RELATIONS OF WATER IN SILICATE MELTS.

The solubility relations of water in glasses of Stone Mountain granite and of albite compositions are very similar and have been described elsewhere.⁸ Some additional data for albite are given in Table III. These data are expressible by hyperbolic equations of the form $x_2 = p/(a + bp)$ where x_2 denotes the concentration of water in weight per cent, p the pressure in bars, and a and b are constants for constant temperature and silicate composition. Values of a and b are given in Table I for albite melt at different temperatures and a plot of these curves in Fig. 2.

TABLE I.

Parameters in the equation $x = p/(a + bp)$ which expresses the weight per cent of water, x , in solution in albite melt as a function of pressure in bars.

Temp. °C.	a	b
900	81.84	0.08458
1000	95.05	0.08715
1100	110.56	0.09008
1200	134.43	0.09100

⁷ Gordon, A. R.: J. Chem. Phys., 2, 69, 1934.

⁸ Goranson, R. W.: This Journal, 22, 481-502, 1931; Trans. Am. Geophys. Union, 17, 257-259, 1936.

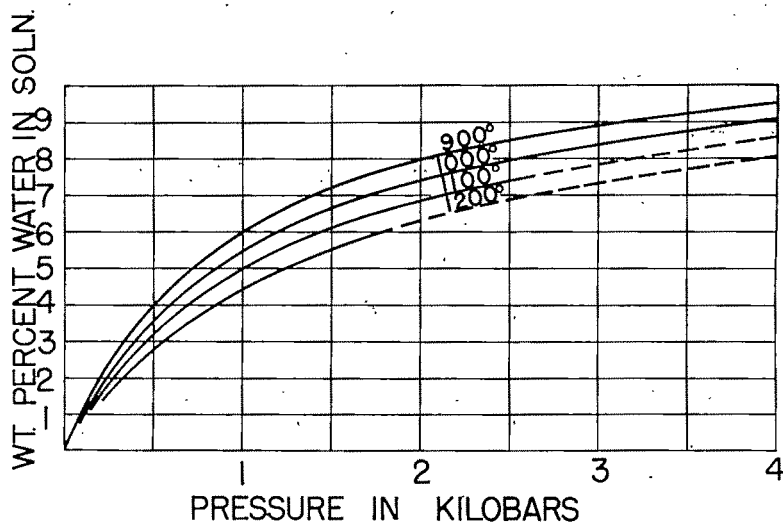


Fig. 2. Solubility relations of water in albite melt in the temperature range from 900 to 1200° C. Weight per cent of water in solution is given by the ordinate and pressure in kilobars by the abscissa.

We have for the concentration-pressure slope of the solubility curve the relation

$$\left(\frac{\partial N_2}{\partial p}\right)_T = \Delta v_2 / \left\{ RT \left[\frac{\partial \gamma}{\partial N_2} \right]_{T, p} + 1 \right\} \quad (2)$$

where N_2 denotes the mole fraction of water in solution, Δv_2 the change in volume when one mole of water goes into solution without change of concentration, R the gas constant, T the absolute temperature, and γ the activity coefficient⁹ of water in solution. For an ideal solution $(\partial N_2 / \partial p)_T = \Delta V_2$.

Now if one assumes that the condensed water phase (the

⁹ The expressions derived herein may be obtained by writing a fundamental equation in the desired variables (R. W. Goranson, *Thermodynamic Relations in Multicomponent Systems*, Carnegie Institution of Washington Pub. No. 408, 1929) for each of the homogeneous parts or phases and then solving the resulting set of equations simultaneously remembering only that for these conditions the temperature, pressure, and chemical potential of a component are the same in each of the phases. For the definition of activity coefficient as used herein see J. Chem. Phys., 5, 107-112, 1937.

analog of liquid water) would occupy the "apparent molal volume" on the hypothesis that it is an ideal solution or, in other words

$$v_{2\text{condensed}} = (\Delta v_2)_{\text{ideal}} - v_{\text{vapor}} = (\bar{v}_2)_{\text{ideal}}$$

$\bar{v}_2 = (\partial V / \partial n_2)$ denoting the "apparent molal volume" or volume which a mole of water would appear to occupy if added to the solution without changing its concentration, i.e. added to an infinite amount of solution, it is then possible to calculate the "condensed specific volume" of the water phase from the solubility slopes and Eqn. (1). The actual apparent molal volume, \bar{v}_2 , may be calculated along the three-phase boundary curve from the expression given later (Eqn. 9) and the equation of state for water (Eqn. 1). The relation between these two calculated quantities namely

$$(\bar{v}_2)_{\text{id}} - \bar{v}_2 = RT (\partial N_2 / \partial p)_T (\partial \gamma / \partial N_2)_{T, p}$$

appears to be approximately constant and given by the expression

$$\bar{v}_2 = (\partial V / \partial n_2) = (0.77_8 \pm 0.03_8) (\bar{v}_2)_{\text{ideal}} \quad (2a)$$

The apparent volume occupied by a gram of water in solution is then 77 per cent of the volume assumed as that of the condensed water phase. A comparison of these quantities is given in Table II. It should be noted here that some of the quantities used in computing these values are not yet very well known as functions of concentration, e.g. Δv_1 and Δh_1 the volume and heat energy changes of the silicate on crystallizing, and that these calculations are to this extent only approximations.

It may be of interest to evaluate the relation $\bar{v}_2 / (\bar{v}_2)_{\text{ideal}}$, found to be 0.77 for the conditions of this investigation, for water-bearing obsidians at room temperature. The Rocche Rosse ($\text{H}_2\text{O} = 0.31\%$; density = 2.370) and Forgia Vecchia ($\text{H}_2\text{O} = 1.01\%$; density = 2.363) rhyolite glasses of Monte Pelato are very similar and may be assumed to be the same except for water content. The ratio of the apparent specific

TABLE II.

Specific volumes and "apparent" specific volumes of water in the two phases vapor and solution. The second column lists the specific volume, $\text{cm}^3/\text{g.}$, of water vapor as calculated from Eqn. (1) for the corresponding temperatures and pressures. The third column lists the "specific volume of the condensed water phase" which is herein defined as the apparent specific volume the water would have in solution were the solution an ideal one. These values are computed from Eqn. (2) for the solubility curves and Eqn. (1). The fourth column lists the true "apparent" specific volume of the water in solution. The relation between the values of columns 3 and 4 were obtained from the freezing-point curves by means of Eqn. (9).

<i>Pressure in bars.</i>	<i>Sp. vol. vapor, v.</i>	<i>Sp. vol. cond. water, (\bar{v}_2)_{ideal}</i>	<i>Apparent sp. vol. water, \bar{v}_2</i>
<i>Temp. 900° C.</i>			
500	10.24	5.575	4.29
1000	5.09	3.62	2.785
1500	3.61	2.895	2.23
2000	3.01	2.59	1.99
2500	2.70	2.42	1.86
3000	2.52	2.32	1.79
3500	2.405	2.255	1.74
<i>Temp. 1000° C.</i>			
500	11.45	6.02	4.63
1000	5.80	4.05	3.12
1500	4.09	3.21	2.38
2000	3.35	2.83	2.18
2500	2.95	2.61	2.01
3000	2.72	2.475	1.905
3500	2.56	2.38	1.83
<i>Temp. 1100° C.</i>			
500	12.61	6.30	4.85
1000	6.47	4.40	3.385
1500	4.55	3.51	2.70
2000	3.68	3.06	2.36
2500	3.205	2.785	2.145
3000	2.92	2.625	2.02
3500	2.73	2.51	1.93
<i>Temp. 1200° C.</i>			
500	13.75	6.44	4.96
1000	7.10	4.44	3.42
1500	4.99	3.69	2.84
2000	4.015	3.235	2.49
2500	3.47	2.95	2.27
3000	3.135	2.765	2.13
3500	2.91	2.63	2.025

volume to the specific volume of water (which is the equivalence of mixing with no change in volume, a criterion of an ideal solution) is

$$\bar{v}_2 = 0.72 (\bar{v}_2)_{\text{ideal}}$$

and this value is in conformity with the result obtained above.

Attention has been called¹⁰ to the fact that for obsidians of high water content the water appears to be present in two forms or phases, some of it in solution in the glass and some of it apparently present as adsorbed water.

The relation above or a similar one based on more comprehensive data could be used as a criterion of water of solution in obsidian glasses. For example, if the specific volume of a glass of high water content did not fall on the curve this fact would indicate that some of the water must be present in a different form. This relation might also permit of a quantitative estimate of the relative proportions of these two kinds of water.

Similarly the molal heat of evaporation, Δh_2 , of the water from the silicate solution may be calculated from the relation

$$\Delta h_2 = -T \left(\frac{\partial N_2}{\partial T} \right)_p \left[RT \left(\frac{\partial \ln Q}{\partial N_2} \right)_{T,p} + 1 \right] = T \Delta v_2 \left(\frac{\partial p}{\partial T} \right)_{N_2} \quad (3)$$

where $(\partial N_2 / \partial T)_p$ denotes the slope of the solubility surface intercept on the concentration-temperature coordinate plane, N_2 being the mole fraction of water in solution. The other quantities are as given for Eqn. (2).

The heat of evaporation increases with increase in temperature and also varies considerably with pressure. A mean value over the temperature-pressure range of this investigation yields about 170 calories per gram but it may vary with temperature and pressure on either side of this mean by as much as 95 cal./g. In this connection an interesting comparison may be made with the heat of evaporation of water at 100° C. which is 539.36 cal./g.

The solubility relations of water in orthoclase melts are complicated by the fact that at pressures below about 2500 bars orthoclase melts incongruently to leucite plus liquid. The data so far obtained indicate that the solubility relations for ortho-

¹⁰ Goranson, R. W.: *Am. Mineral.*, 22, 490, 1937; *Trans. Am. Geophys. Union*, 18, 247, 1937.

clase melt roughly parallel the curves for albite melt but are displaced toward the pressure axis by about 1.5 to 2 weight per cent of water; in other words water is less soluble in orthoclase melt by a mean value of about 1.8 weight per cent. These results are in approximate agreement with a previous determination on a 25 quartz—75 orthoclase-mixture.

FREEZING-POINT RELATIONS IN THE ALBITE-WATER SYSTEM.

Albite melts at $1115 \pm 5^\circ \text{C.}^{11}$ at atmospheric pressure and with an estimated volume increase, Δv_1 , of 0.039 cm.^3 per gram. The heat of melting has not been experimentally determined but may be computed from the solidus-liquidus curves in the system albite-anorthite¹² as 203 joules per gram from the

$$\Delta h_1 = \frac{RT_0 T}{M_1(T_0 - T)} \ln \frac{N_1}{N_1'} + \Delta \bar{C}_{P_1} (T_0 - T) \text{ j/g.} \quad (4)$$

ideal solution equation where Δh_1 denotes the heat of melting of albite, M_1 its effective molar weight, N_1 and N_1' the mole fractions of albite in the solidus and liquidus phases respectively, T the absolute temperature, T_0 the freezing point of the pure component "1," $\Delta \bar{C}_p = \bar{C}_p' - \bar{C}_p$ the mean heat capacity of the two phases between T_0 and T , and $R = 8.315$ the gas constant. Although the equation (4) is valid only for ideal solutions so that, in general, only initial slopes can be utilized, it has been our experience, from published data and theoretical considerations, that systems such as albite-anorthite which are miscible in all proportions in the solid as well as liquid state are the best examples we have of ideal solutions.

Increase in pressure will therefore raise the melting temperature of anhydrous albite and this initial rise may be computed from the Clapeyron equation, $(dT/dp) = T\Delta v_1/\Delta h_1$, to be 26°C. per kilobar. Δh_1 and Δv_1 are functions of pressure so that, in order to calculate the slope at higher pressures, they must be evaluated accordingly.

When water is a constituent of the system there are three phases present along the albite freezing-point curve, namely vapor essentially of water, a solution of water in silicate melt,

¹¹ Private communication from J. F. Schairer.

¹² Bowen, N. L.: This Journal, 35, 583, 1913. His calculated heat of melting agrees with the value adopted here.

and albite crystals. The experimental data are given in Table III and plotted in Figs 3 and 4.

TABLE III.

Experimental Data for the System $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$.

The first two columns list the pressure in bars and temperature in deg. C. of the run. The third column lists the state of the silicate component after quenching. The fourth column lists the weight per cent of water in solution in the silicate melt.

Pressure in bars	Temp. in °C.	State of silicate	Wt. % water in solution
300	1040	glass	2.8 (high)
500	1030	glass	3.2, 3.2
509.5	960 ± 4	few xls. mostly glass	
	956 ± 5	xls.	
517	1000 ± 4	glass	3.65, 3.58
656	970 ± 5	glass*	4.45
(788)	1000 ± 7	glass**	3.54, 2.78, 2.6
790 ± 9	950	glass	5.8 (high)
887	905	xls.	
1000	1055 ± 10	glass	5.3
1000	1010	glass	5.45, 5.65
1000	950	glass	5.3, 5.5
1007 ± 9	910 ± 5	glass	5.8, 5.8
1146	910 ± 5	glass*	6.9 (high)
1220 ± 37	1010 ± 10	glass*	5.8, 5.9, 5.9
1245 ± 4	915	glass*	7.22, 7.22, 7.12 (high)
1250 ± 50	1000 ± 10	glass*	6.8, 6.8, 7.0, 6.8 (high)
1260	1200	glass*	4.8, 5.0, 5.0, 4.9
1262	1110	glass*	5.2, 5.2, 5.4
1315	905	glass*	7.5 (high)
(1413)	905	xls.**	4.13, 4.46
1450	910	glass	7.5, 7.3
1483 ± 60	810	xls.	
1535	845	xls.	
1567	849 ± 3	xls.	
1600	1050	glass	6.72
1694	1000	glass	7.15, 6.85
1700	847	xls.	
1700	860	glass	7.54
1770	910	glass	7.8, 7.8, 8.0, 8.2 (high)
2380	1110	glass	7.3, 7.6, 7.5
2414	830	glass*	8.8; 7.9, 7.8, 8.2 (low)
2414	830	xls.	
2575	1015	glass	8.0
2725	955	glass	8.48, 8.72, 8.49, 8.47
2772 ± 90	815 ± 5	xls.	
2813 ± 100	910 ± 10	glass	8.7, 9.0
2983	1020	glass	8.3, 8.45
3288	905 ± 5	glass	8.85, 8.85, 8.7, 8.87

* Indicates one set of charges consisted of ab. glass plus water and one set of ab. glass plus ab. xls. plus water.

** Indicates that the charges were unsaturated with respect to water.

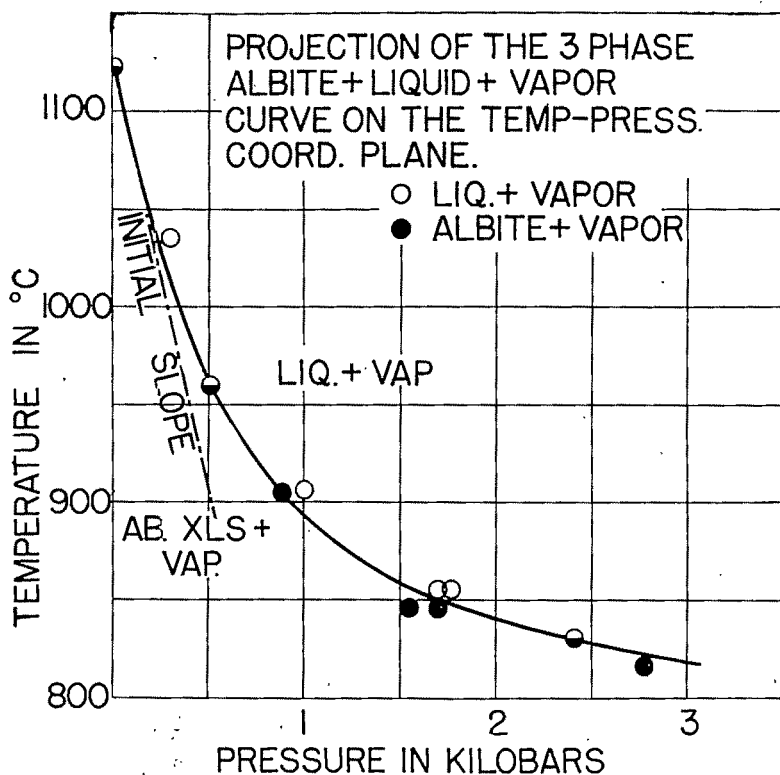


Fig. 3. The projection of the freezing-point curve of albite in the albite-water system on the temperature (ordinate)-pressure (abscissa) coordinate plane.

The equation expressing the slope, dT/dp , of the three-phase equilibrium curve projected on the temp.-press. coordinate plane is

$$\frac{dT}{dp} = \frac{T[\Delta v_1 - x_2(\Delta v_1 + \Delta v_2)]}{\Delta h_1 - x_2(\Delta h_1 + \Delta h_2)} \quad (5)$$

where subscripts 1 and 2 refer to the components albite and water respectively, Δv_1 and Δh_1 denote the volume decrease and heat evolved respectively per gram of albite on crystallizing from solution, Δv_2 and Δh_2 denote the volume increase and heat absorbed respectively per gram of water on evaporating from solution, x_1 and x_2 denote the weight fractions of albite and water resp. in the solution, and T denotes the absolute tem-

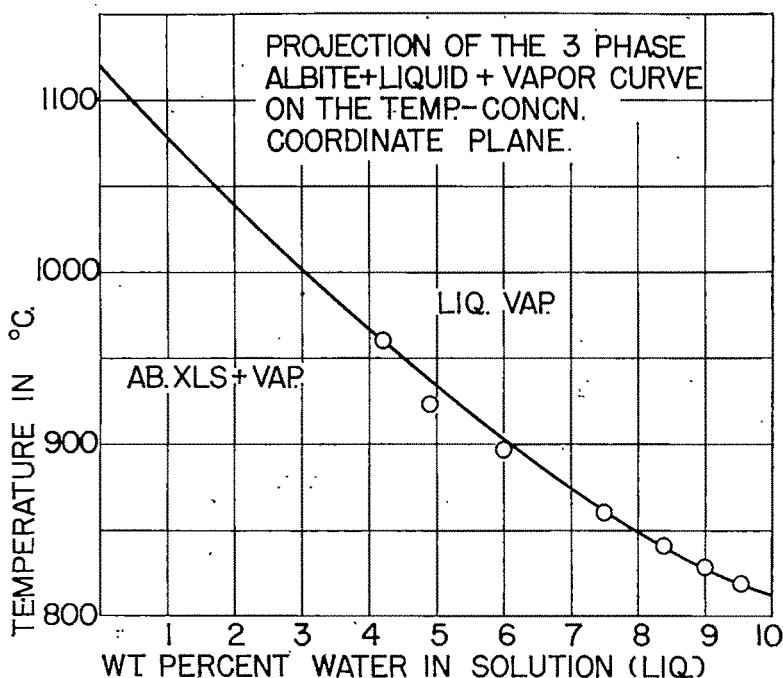


Fig. 4. The projection of the freezing-point curve of albite in the albite-water system on the temperature-concentration coordinate plane. Temperature is given along the ordinate and concentration of water in weight per cent along the abscissa.

perature. As may be observed this expression will reduce to the Clapsyron equation by making $x_2 = 0$.

The initial slope, dT/dp , of the freezing-point curve of anhydrous albite was calculated to be 2.6° per hundred bars. The initial freezing-point slope, dT/dp , of albite in the albite-water system is calculated from the equation

$$\lim_{x_2 \rightarrow 0} \frac{dT}{dp} = \frac{T}{\Delta h_1} \left[\Delta v_1 - \frac{RT}{M_2} \lim_{x_2 \rightarrow 0} \frac{x_2}{p} \right], \quad (6)$$

where M_2 is the molar weight of water and the quantity

$$\lim_{x_2 \rightarrow 0} \frac{x_2}{p}$$

is evaluated from the solubility curves; to be -40.24° per hundred bars. The effect of increase in pressure for the latter

system is therefore to lower the freezing temperature of albite, and the difference between the two slopes, i.e. for the anhydrous and hydrous systems, is 43° per hundred bars.

The slope of the freezing-point curve projected on the temperature-concentration coordinate plane is given by the equation

$$\frac{dT}{dx_2} = - \frac{T[\Delta v_1 - (x_2/x_1)\Delta v_2] (\partial p/\partial x_2) T}{T \Delta v_1 (\partial p/\partial T)_{x_2} - \Delta h_1} \quad (7)$$

The initial slope is therefore

$$\lim_{x_2 \rightarrow 0} \frac{dT}{dx_2} = \frac{T}{\Delta h_1} \left[\Delta v_1 \left(\lim_{x_2 \rightarrow 0} \frac{p}{x_2} \right) - \frac{RT}{M_2} \right] \quad (8)$$

and is evaluated as -41.4° per weight per cent of water. This slope is plotted as a dashed line in Fig. 4.

In order to realize a maximum pressure on the crystallization curve, i.e. to have the curve become tangent to the pressure axis, dT/dp must become infinite or

$$\Delta h_1 = (x_2/x_1) \Delta h_2 = (x_2/x_1) T (\partial p/\partial T)_{x_2} \Delta v_2$$

which occurs neither in the systems examined here nor in the "granite-water" system¹⁸ and therefore, so far as is now known, does not occur for the rock-forming silicate systems.

In order to realize a minimum temperature on the crystallization curve, i.e. to have the curve become tangent to the temperature axis, dT/dp must become zero or

$$\Delta v_1 = (x_2/x_1) \Delta v_2.$$

Now there are two opposing effects, one tending to raise the freezing point—initially 26° per kilobar—and the other to lower the freezing point—initially 402° per kilobar. As is apparent from Figs. 3 and 5 the slope $-(dT/dp)$ decreases with increasing pressure. The reason for this is that the latter effect decreases with increasing pressure because, even though the concentration x_2 increases with pressure although at a diminishing rate, Δv_2 decreases and eventually the numerator of Eqn. (5) may become zero and the curve begin to rise with still further increase in pressure.

¹⁸ Goranson, R. W.: This Journal, 23, 227-236, 1932.

The apparent specific volume \bar{v}_2 of the water in solution along the freezing-point curve may be computed from the equation

$$\bar{v}_2 = v - \left[\frac{\Delta v_1 - (\Delta h_1/T)(dT/dp)}{(x_2/x_1)\{1 - (dT/dp)(\partial p/\partial T)_{x_2}\}} \right] \quad (9)$$

where v denotes the specific volume of water in the vapor phase and is calculated from Eqn. (1), dT/dp the temp.-press. slope of the freezing-point curve, $(\partial p/\partial T)_{x_2}$ the press.-temp. slope of the solubility curve at constant concentration, and the other quantities are as previously defined.

The quantities Δv_1 and Δh_1 , the volume decrease and heat evolved when a gram of albite crystallizes from the solution (at constant concentration), are functions of concentration but, since these relations are not known explicitly, Δv_1 is assumed as constant and Δh_1 is only partially corrected in the computations which establish the relationships of Eqn. (2a) and the tabulated values of column 4, Table II.

If we divide the heat of evaporation of water from the silicate solution into two parts, an internal and an external heat, such that

$$\Delta h_2 = (\Delta h_2)_{\text{int.}} + p \Delta v_2$$

it is found that the internal heat of evaporation, $(\Delta h_2)_{\text{int.}}$ along the f.p. curve varies about 10% from a mean value of 240 joules per gram of water whereas the external heat of evaporation, $(\Delta h_2)_{\text{ext.}} = p \Delta v_2$, decreases steadily with increasing pressure.

FREEZING-POINT RELATIONS IN THE SYSTEM, $\text{KAlSi}_3\text{O}_8\text{-H}_2\text{O}$.

This system is more complicated than the $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ system in that at atmospheric pressure orthoclase (KAlSi_3O_8) melts incongruently to leucite (KAlSi_2O_6) and liquid at about 1120 ± 20 ,¹¹ the leucite in turn melting to form liquid of KAlSi_3O_8 composition at 1535°C .

The experimental results are given in Table IV and a projection plot of this data on the temp.-press. coordinate plane for the vapor-liquid-solid curves in Fig. 5.

The incongruent melting curve as plotted seems to be somewhat high and should perhaps extrapolate to about 1100° at atmospheric pressure. Some further data are being obtained

for this curve and for the solubility relations of the melt in equilibrium with leucite. Further calorimetric and volumetric data are also needed in order to evaluate the thermodynamic properties of this system. It is of interest to note, however, that the stability field of leucite becomes wiped out at about 2500 bars, the orthoclase melting congruently above this pressure.

TABLE IV.

Experimental Data for the System, $\text{KAlSi}_3\text{O}_8\text{-H}_2\text{O}$.

The first two columns list the pressure in bars and temperature in deg. C. of the run. The third column lists the state of the silicate after quenching. The fourth column lists the weight per cent of water in solution in the silicate melt.

<i>Pressure in bars</i>	<i>Temp. in °C.</i>	<i>State of silicate</i>	<i>Wt. % water in solution</i>
500	1030	leucite alt. to or.*	
1000	955	or. after lc.	
1000	1007 ± 7	leucite glass	
1000	1060	leucite glass	
1000	1085	leucite glass	
1007	1128 ± 5	leucite glass	
1007	1137 ± 10	glass	
1000	1140	glass	
1020	1145	glass	
1550	965	or. xls.	
1600	1035	leucite glass	
1600	1040	glass	
1900	995	leucite glass	
1900	1000 ± 5	glass	
2053	953 ± 5	intergrowth lc. + or.	
		(or. seems to be repl.* lc.)	
2055	1015 ± 5	glass	} 5.86 (mean of five determinations)
2060	1010	glass	
2185	975	glass	
2372	968	glass	
2486	960	glass	
2616	960	glass	5.97, 5.97
2622	950	all or. xls.	
2725	950	or. xls.	
2725	960	glass	
2813	897	or. xls.	
2983	1000	glass	6.2, 6.4
(3290)	905	or.**	0.4**
3300	939	glass	
3360	960	glass	6.875
3400	948	glass	
3400	938	glass	
3582	940	glass	6.68
3636	934	or. xls.	
3640	937	glass	7.08

* or. xls. denotes orthoclase crystals; lc. indicates leucite.

** Indicates the system was unsaturated because of a leak.

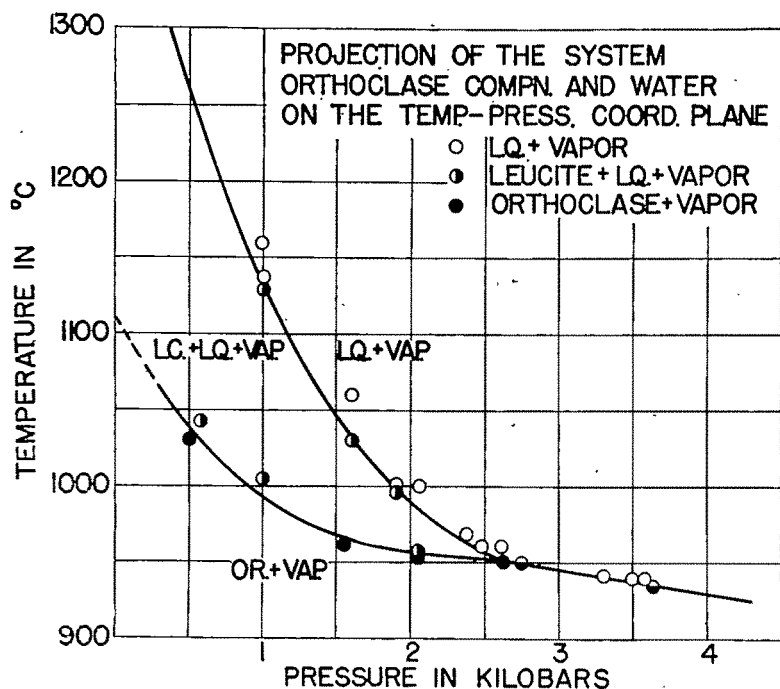


Fig. 5. Freezing-point curves in the system, orthoclase composition and water projected on the temperature-pressure coordinate plane. The lower curve from 0.001 to 2.6 kilobars pressure is the incongruent melting curve of orthoclase. Above 2.6 kilobars orthoclase melts congruently and the leucite field has disappeared.

GENERAL CONSIDERATIONS.

In order to demonstrate the tremendous pressures that may be built up in such systems as these on cooling and crystallizing let us assume we have an albite-water solution at a pressure of 606 bars (corresponding to a depth of about $2\frac{1}{4}$ km.) and temperature of 1100°C .; the water content of this solution at saturation is 4.2 weight per cent. Now let the solution cool—it will at first follow a line of slope $(\partial T/\partial p)_{x_2} = 1.32$ in Fig. 3 so that when it has reached the projected freezing-point curve, i.e. when the temperature has fallen to 960° , the pressure will have dropped to 500 bars. At this stage albite will begin to crystallize from solution and, if the enclosing chamber walls of the silicate-water melt are impervious and competent to retain the pressure developed, the system will move along

the freezing-point curve. When the temperature has fallen an additional 59° , i.e. to 819° C., the pressure will have increased sixfold to a value of 3000 bars. At this stage the system will consist of 56 per cent albite crystals and a melt containing 9.5 per cent water (see Fig. 4) if we neglect the amount of water that must be evaporated to build up this pressure.

Again if we have a melt saturated with water at 900° C. and 1000 bars pressure and let the temperature fall 81° , i.e. to 818° , under the same conditions as above the pressure will have risen threefold to 3000 bars. At this stage the system will consist of 37.2 per cent albite crystals and 62.8 per cent melt containing 9.5 per cent water.

If there is no minimum temperature on the freezing-point curve this development of pressure can continue until all the albite has crystallized. If a minimum freezing-point temperature exists then the pressure corresponding to this temperature will be the maximum that can be developed by cooling with crystallization. However, such a minimum must correspond to a pressure exceeding 4000 bars and perhaps 5000 bars as judged by the probable prolongation of the curve. Because of the limited miscibility relations no pressure maximum exists on the freezing-point curve.

In a previous paper¹³ the liquidus curve for granite in the system "granite-water" was extrapolated to atmospheric pressure by an incorrect analogy. Extrapolation based on the systems studied herein would put the liquidus temperature of granite at atmospheric pressure as about 950° which is 100° lower than the previous estimate. This value seems not unreasonable and not inconsistent with the results of Greig, Shepherd, and Merwin¹⁴ who found that in one week at 800° powdered granite became half liquid. The projected liquidus curve on the T - p coordinate plane for a granite-water system will be a discontinuous one but, as judged from the similarity to the albite-water system in solubility relations and from the few freezing-point measurements made, should roughly correspond to the crystallization curve of the latter with the exception that corresponding temperatures will be about 200° lower in the granite-water system. This development of pressure on crystallization should therefore be directly applicable to a

¹⁴ Carnegie Inst. of Wash., Year Book No. 30, 77-78, 1931.

hydrous granite magma and thus indicates a very potent source of pressure development for explosive igneous activity.

This picture may be compared with that suggested by Morey¹⁵ who used as analogy the system, $\text{H}_2\text{O}—\text{K}_2\text{SiO}_3—\text{SiO}_2$, studied by Morey and Fenner. They found that a maximum pressure of 340 bars existed on the freezing-point curve of the mixture KHSi_2O_6 and quartz, i.e. a point where $dp/dt = 0$, which does not exist in the systems studied by the writer. In the example used by Morey the maximum pressure that could be developed would then be of the order of 340 bars instead of the thousands of bars pressure realized herein.

In the orthoclase composition—water system, if we start with a melt at 1130° and 1000 bars and let the system cool in a competent chamber, leucite will crystallize and the system move along the liquidus curve, the solution increasing in water content and decreasing in silica content until it reaches a pressure of about 2600 bars and 955° . At this point leucite will redissolve and orthoclase crystallize from the solution. On further cooling orthoclase will continue to crystallize and at 930° the pressure will have increased fourfold to 4000 bars. If the chamber were not competent to withstand more than 1000 bars internal pressure, then the system instead of following the liquidus curve would follow the 1000 bar isopiestic line with leucite crystallizing out until a temperature of approximately 990° was reached, at which point orthoclase would separate out and leucite redissolve if cooling were slow enough; if the cooling rate were rapid at this point then one would obtain a glass studded with leucite crystals.

¹⁵ Morey, G. W.: J. Wash. Acad. Sci. 12, 219-230, 1922.

THE SYSTEM, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
(NEPHELITE, CARNEGIEITE)— $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
(ALBITE).

J. W. GREIG AND TOM. F. W. BARTH.

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ABSTRACT.

The results of an experimental study of equilibrium in the system, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ — $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, are summarized in an equilibrium diagram, Fig. 1, and some of the relations to other systems are indicated in another diagram, Fig. 2.

INTRODUCTION.

This paper presents the results of an experimental investigation of phase equilibrium relationships in the system, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (nephelite, carnegieite)— $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (albite), at atmospheric pressure, over a range of temperature of about 500°C ., within which all the melting phenomena occur. The results are summarized and shown graphically in an equilibrium diagram, Fig. 1, and the principal data, on which the diagram is based, are collected in tabular form.¹ The relationships in this system, with albite as one end member, are similar to those found in the corresponding system, in which

¹ In this paper, temperatures are expressed in terms of the scale established by Day and Sosman (Day, A. L., Sosman, R. B., and Allen, E. T.: Carnegie Inst. Washington, Publ. No. 157, 1911) using the curve fitted to their data by Adams (Adams, L. H.: J. Am. Chem. Soc., 36, 65-72, 1914). The scale differs from the "International Temperature Scale." Several estimates of the differences between the two scales have been published, e.g. Wensel, H. T., and Roeser, W. F.: Bur. Standards Journal of Research, 5, 1309-1318, 1930; Sosman, R. B.: J. Am. Ceram. Soc., 16, 54-57, 1933. In the temperature region with which this paper deals, values of temperatures expressed in terms of the "International Temperature Scale" are probably always slightly higher than values for the same temperatures expressed in terms of the scale of Day and Sosman.

the place of albite is taken by anorthite, the other end member of the plagioclase series.²

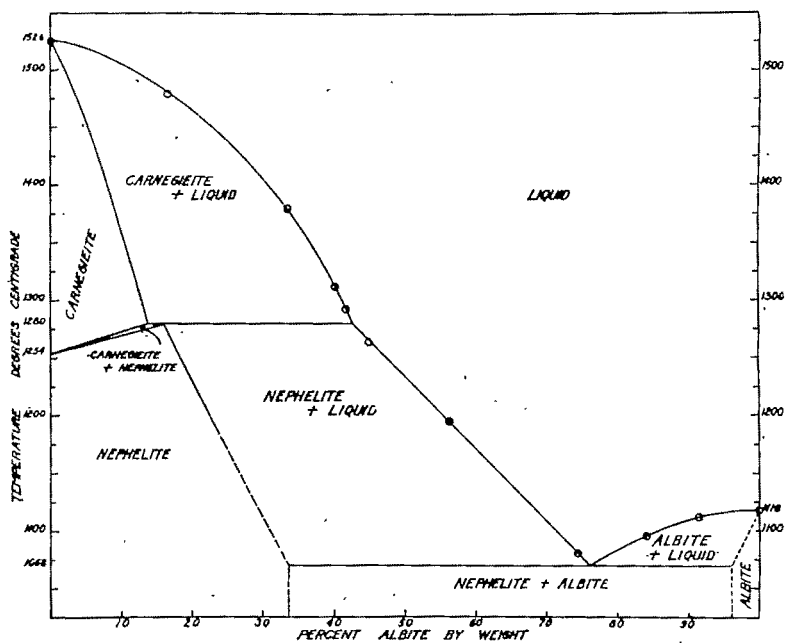


Fig. 1. Equilibrium diagram for the system, $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.2\text{SiO}_2$ (nephelite, carnegieite)— $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.6\text{SiO}_2$ (albite). The circles indicate determination of points on the liquidus. For other data see tables.

No discussion of the relationships shown on the equilibrium diagram seems called for, as similar systems have been published before, and no discussion is given here. In the pages that follow, however, a number of points in the experimental work are discussed in more or less detail.

EXPERIMENTAL.

Preparation of Glasses.

The first step in the experimental work was the preparation of a series of homogeneous glasses. The raw materials used were:

Silica, a crushed quartz, which after evaporation with hydrofluoric and sulphuric acids leaves a residue of less than 0.04 per cent, was converted to cristobalite by firing it at a high temperature.

² Bowen, N. L.: This Journal, 33, 551-573, 1912.

Alumina, prepared from the distilled chloride by a double precipitation with hydrochloric acid gas and ignition of the resulting aluminum chloride six hydrate.

Soda, weighed as the carbonate. The source was a particularly good sodium carbonate monohydrate. An analysis by E. G. Zies gave: SO_3 <0.001 per cent, Cl <0.001 per cent, SiO_2 <0.002 per cent, $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ 0.003 per cent, CaO 0.008 per cent, MgO none.

Instead of making up each glass directly from these materials, a preparation, containing about 35 per cent soda 65 per cent silica, was made up and used as a source of soda in preparing the ternary glasses, the purpose being to avoid, as far as practicable, loss of soda during the melting of the glasses. This preparation was made in an electric furnace with a maximum temperature of 1050°C . At this temperature the liquid retains a good deal of gas.³ This was driven off by crystallizing the material. Careful weighing showed that after the gas had been driven off, and before the charge was crushed, the weight was that of the soda and silica originally put into the charge. Several analyses were made on these materials, and they agreed with the compositions as determined by synthesis. There was then no detectable loss of soda.

In preparing the ternary glasses some soda is volatilized from the more sodic glasses while they are being heated at high temperatures. In order to keep track of the composition, careful weighings were made to detect any changes of weight that might occur while the preparations were in the furnace. These glasses take up some moisture from the air during crushing.⁴ After crushing, the charge was heated in an electric furnace in air at 900° , and any loss taken to be water. Subsequent loss, at higher temperatures, was taken to be soda. With increase in silica the loss during heating decreases. Charges of 10 grams of albite glass showed no loss after being heated for 3 hours at 1650° – 1675° .

In general, the compositions of these glasses do not lie exactly in the binary system, but, neglecting impurities, are expressible in terms of Na_2O , Al_2O_3 , and SiO_2 . The composi-

³ This material, after being prepared in the electric furnace in air, increases in weight if heated over a meker burner (900° – 1000°C .), presumably by dissolving gases from the flame.

⁴ For an interesting series of data on the moisture taken up by powdered feldspar crystals and glasses see A. L. Day and E. T. Allen: *Isomorphism and Thermal Properties of the Feldspars*, p. 57, Carnegie Inst. Washington, Publ. No. 31, 1905.

tions were plotted on a ternary plot, and from the points representing the compositions perpendiculars were drawn to the binary join. The intersections of these perpendiculars with the binary join give the compositions stated in the tables. These perpendiculars are, in all cases, so short that no significant error could be introduced into the liquidus relationships by the indicated departure of the composition from the binary system. The chief effect is likely to be the persistence of some residual liquid when an attempt is made to crystallize a mixture completely.

Melting Temperature of Albite.

The investigation of silicate equilibria dates properly from the work of Day and Allen on the feldspars.⁵ In that work they began their melting determinations on anorthite. By making heating curves on the crystalline material they were able to determine the melting point. But, as they extended their investigation to more albitic feldspars, they found that the discontinuity on the heating curves was spread out to such an extent that the method gave no well defined melting temperature, and before albite was reached, gave no results at all. This led them to study the character of the change from the crystalline to the liquid state in the alkali feldspars. By holding the material at a constant temperature, for a long period of time, then cooling it, and examining the product with the microscope, they were led to recognize, for the first time, the existence of materials that can persist, in the crystalline state, for considerable periods of time at temperatures far above their melting temperatures, and that melt with extreme slowness in the lower portion of this range of instability. These observations have been abundantly confirmed since that time, and experience with silicates leads to the belief that the persistence in the crystalline state at temperatures above the melting temperature is a general property of silicates, and probably of matter, the differences being of degree.

Day and Allen found traces of melting in natural albite as low as 1100°, but were not able to establish a melting temperature. They say (op. cit., p. 50): "We did not extend any single trial beyond a single day, so that our results can not pretend to establish the lowest point at which albite melts.

⁵ Op. cit.

Such an effort with a natural specimen known to contain impurities would yield nothing of value."

Bowen,⁶ some years later, made a study of the plagioclase feldspars, determining the melting intervals of the series and drawing up an equilibrium diagram. Like Day and Allen, he was unable to crystallize albite, so used natural material. He found traces of glass after one hour at 1105° and no change after 2 hours at 1089° . He placed the temperature of the solidus for this material at $1100^\circ \pm 10^\circ$ and the melting point of pure albite at the same temperature. We have not repeated this work on natural albite, our experiments being confined to synthetic material. The value of the melting point that we obtained is higher than this; 1118° , and the sluggish nature of the reactions in our material leads to the suspicion that the material that Bowen had was inhomogeneous.

The melting temperature of a crystalline substance, that melts congruently, is the temperature at which it can coexist in equilibrium with a liquid of the same composition. Above this temperature, the equilibrium state is one of complete liquidity, below it, of complete crystallinity. With some substances these reactions proceed so rapidly that they are not heated significantly above their melting temperatures without melting. In such cases failure to melt at a given temperature is sufficient indication that the temperature is below the melting temperature. However, with materials like albite, that melt to very viscous liquids, though melting at a given temperature shows that that temperature is above the melting temperature, failure to obtain melting does not show that it is not. Growth of crystals, on the other hand, does show that the temperature at which the growth occurs is below the melting temperature. We have fixed the melting temperature of pure albite, within limits, by finding a temperature at which crystals of albite melt to an albite liquid, and a second temperature at which they grow in an albite liquid. This was done by first growing small crystals of albite in a homogeneous glass of albite composition. The material, so prepared, was then held for some time at a constant temperature, then, by using the microscope, compared with the original material. If necessary, the heating time was increased until there was an unmistakable change in the size of the albite crystals. In this way a bracket was established. Then, by making longer runs, the bracket was

⁶ Bowen, N. L.: This Journal, 35, 577-599, 1913.

TABLE I.
Melting points of albite.

Temp. °C.	Original condition	Time	Result
1113°	Crystals in glass	3 days	Crystals have grown
	Crystals	3 days	No change
1116°	Crystals in glass	2 days	Can see no change
1122°	Crystals in glass from run at 1113° above	1 day	Can see no change
		2 days	Crystals are smaller
		3 days	Nearly all glass
	Crystals	1 day	A little interstitial glass
		2 days	Glass increasing
A bracket 1113°-1122° is established by these runs.			
1126°	Crystals in glass	1 day	All glass
	Crystals	1 day	Films of glass between the crystals throughout the charge
		2 days	Charge now contains only a few per cent of crystals. The smaller crystals have melted.
		3 days	Crystals have decreased
		4 days	Traces only of crystals
1115°	Crystals in glass	7 days	Crystals have grown
1120°	Crystals in glass	7 days	All glass

The melting temperature lies between 1115° and 1120°, probably at 1118°.

narrowed.⁷ The results of these runs are listed in Table I, and the final bracket appears again in Table II.

The preparation of material suitable for these runs required considerable experimentation. We grew crystals of albite in the powdered albite glass in air but did not use them for the final work, for we found that by growing them under a small pressure of water vapor in sealed tubes of silica glass, we had a much better choice of size and distribution of crystals. In the same way we also prepared crystalline albite free from all but small traces of glass. Powdered albite glass was placed in a crucible of platinum foil, and the platinum folded down tightly over the charge, sealing it in. The charge, together with a source of water, was then sealed in an evacuated tube of silica glass and heated in an electric furnace. As a source of water we used gibbsite in some cases, and a rhyolitic glass

⁷ These runs were possible only through automatic controlling and recording of the temperature. The control was by means of a regulator of the type due to White and Adams (Phys. Rev., 14, 44-48, 1919) and adapted by Roberts to use on alternating current. See especially J. Opt. Soc. Amer. and Rev. Sci. Instr., 11, 171-186, 1925. The recording potentiometer was built for this Laboratory by Leeds and Northrup.

TABLE II. Liquidus of carnegieite, of nephelite, and of albite.

Per cent albite by weight	Temp. °C.	Time	Original condition	Condition after runs
0.0	1524	30 min.	Glass	Glass + some carnegieite
0.0	1527	30 min.	Carnegieite	Carnegieite
		30 min.	Glass	Glass
		60 min.	Carnegieite	Glass with trace of carnegieite
			Carnegieite	Glass
The melting point is closer to 1527° than to 1524°, therefore at 1526°				
16.0	1476	60 min.	Glass	Glass with carnegieite
	1480	60 min.	Glass	Glass
33.5	1374	60 min.	Glass + carnegieite	Glass
		60 min.	Glass + carnegieite	Glass + carnegieite
40.2	1307	60 min.	Glass + carnegieite	Glass + carnegieite
		120 min.	Glass + carnegieite	Glass + carnegieite
		75 min.	Glass + carnegieite	Glass + carnegieite
41.7	1316		Glass	Glass
		120 min.	Glass	Glass
	1289	120 min.	Glass	Glass + carnegieite
	1297		Glass	Glass + trace carnegieite
45.1	1256	150 min.	Glass + nephelite	Glass + trace carnegieite
	1260	150 min.	Glass + nephelite	Nephelite crystals grown
	1264	150 min.	Glass + nephelite	No definite change
56.4	1190	17 hrs.	Glass + nephelite	Glass
		5 hrs.	Glass + nephelite	Nephelite crystals grown larger
74.3	1072	48 hrs.	Glass + nephelite	Nephelite almost all gone
	1080	48 hrs.	Glass + nephelite	Nephelite has grown
	1089	24 hrs.	Glass + nephelite	Can see no change
	1088	72 hrs.	Glass + nephelite	Nephelite all gone
84.2	1097	48 hrs.	Glass + albite	Albite grown
		48 hrs.	Glass + albite	Albite slightly smaller
	1101	48 hrs.	Glass + albite	All glass
91.6	1102°	24 hrs.	Glass + albite	Albite grown
	1110	96 hrs.	Glass + albite	No change seen
	1115	19 hrs.	Glass + albite	Albite nearly all melted
100.0	1115+	168 hrs.	Glass + albite	Albite crystals grew
	1120—	168 hrs.	Glass + albite	All glass

containing about 3 per cent of water in others. Under these conditions some volatilization of silica from the walls of the tube occurs, but there is no detectable contamination of the charge inside its platinum container.⁸

Before any of these materials were used for the equilibrium investigations, the finely powdered materials were heated in air, close to the melting temperature, for 24 to 48 hours to make sure that they were dry.

Merwin⁹ had, some years before, found that some change takes place in natural albite crystals, when they are heated in the neighborhood of 900°, and that it takes place in a few hours. As the duration of our runs was always several times as great as this, we did not expect any difference in the behavior of crystals grown at different temperatures. However, we tried crystals grown at 800°, 930°, and 1000°, but found no differences in behavior.

It will be seen from the data of Table IV that crystals of albite in an albite liquid persist for long periods of time at temperatures above the melting point. Thus after four days at 1126°, some crystal remnants still persist. A microscopic examination of the charges, that were held at temperatures above the melting point, shows that, at these temperatures (no experiments were made at temperatures far above the melting point), the melting occurs at the surfaces of crystals. The crystals gradually become smaller in size. The length of time required to melt a charge of albite at a given temperature depends therefore on the size of the individual crystals. These crystals in contact with a liquid of their own composition behave exactly like the same crystals in a somewhat different liquid when held just above the temperature of the liquidus, e.g. the albite crystals in the 91.6 per cent liquid at 1115° (see Table I). This is in agreement with Day and Allen's observations on the natural crystals, that the melting took place along cleavages. It is of interest in this connection, that quartz, which, like albite, may persist far above its melting temperature,¹⁰ likewise melts at the surface, at least over a considerable range of temperatures above the melting temperature.

⁸ Greig, J. W., Merwin, H. E., and Shepherd, E. S.: *This Journal*, 25, 61-73, 1933.

⁹ Merwin, H. E.: *J. Wash. Acad. Sci.*, 1, 59-60, 1911.

¹⁰ This was reported by Ferguson and Merwin (*This Journal*, 46, 417-426, 1918) and has been repeatedly observed by one of us. An extreme example may be cited. A particularly fine quartz crystal was heated to about 1800° C. in an effort to melt it quickly. After cooling, it was found that the outer portion was silica glass but the inner part was still crystalline quartz.

Melting Temperature of Carnegieite.

The melting temperature of albite was located by showing it to be below one temperature, at which the crystals melted, and above another temperature, at which crystals grew. The melting temperature of carnegieite has also been bracketed, but, that the lower of the two temperatures is below the melting temperature, is shown in a somewhat different way. If a charge of powdered glass, of the composition of carnegieite, weighing a few hundredths of a gram,¹¹ is plunged into a furnace, already at the melting temperature of carnegieite, and is quenched shortly before the charge reaches this temperature, it will be found, on microscopic examination, that there is no visible glass. The crystallization, however, is spherulitic, and presumably there is interstitial glass. If, instead of quenching such a charge, it is held just under the melting temperature, or, if the quenched charge is returned to the furnace, and held at that temperature, liquid will collect, and large solid crystals of carnegieite will grow in it. The charge, originally glass, of the first run listed in Table II is an example.

Although the rate of approach to equilibrium, when carnegieite is heated just above its melting temperature, is slow enough so that it can be held there for an appreciable time without melting completely, it is in marked contrast with the rate at which equilibrium is approached when albite is so treated. So rapid indeed is this approach that Bowen¹² was able to determine the melting point by making heating curves, and the temperature so determined agrees with the temperature determined by the runs listed in Table I. No doubt this *exact* agreement is fortuitous, but it serves to illustrate the remarkable difference in behavior of carnegieite and albite near their melting temperatures—a difference very similar to that found by Day and Allen between the behaviors of anorthite and albite.

Liquidi of Albite, Nephelite, and Carnegieite.

A point on the liquidus of a crystalline phase represents the temperature and composition of a liquid that can coexist in

¹¹ A typical charge might weigh 0.035 grams and be held in a flat envelope of platinum foil weighing about 0.06 grams and measuring 6 x 8 mm.

¹² Bowen, N. L.: This Journal, 33, 551-573, 1912. Two heating curves gave 1525° and 1527° respectively; he therefore placed the melting point at 1526°.

equilibrium with the crystals. Experiments determining two such points, the melting points of albite and of carnegieite, have been described above. The growth or melting of crystals, in the experiments by which these special points were located, is a simpler process than it is in similar experiments, made on materials of intermediate compositions. In the general case, in which melting at equilibrium takes place, not at one temperature, but over a range of temperatures, the crystals grown in the liquid, preparatory to the determination of a point on a liquidus, may or may not be of the same composition as the liquid itself, but the composition of the crystals, that can coexist in equilibrium with the liquid, is always different from that of the liquid. The total mass of the small crystals, that are developed in the liquid, in order to make the determination, is so small that their formation changes the total composition of the remaining liquid by an amount that is equal to but a small fraction of the uncertainty in the composition of the liquid. This change in total composition of the liquid is therefore negligible. However, it is not the bulk composition of the liquid, but the composition of that liquid immediately surrounding the crystals at any given time, that determines the direction of change in the crystals. An analysis of the different possibilities shows that some melting of these crystals may take place at a temperature below that of the liquidus, but that complete melting cannot do so. On the other hand, provided the material has not been heated at a temperature above that of the liquidus, growth of the crystals can only take place at temperatures below that of the liquidus. The temperature of the liquidus, for any given composition, may then be bracketed by finding a temperature, at which crystals, grown in an originally homogeneous liquid of that composition, are completely melted, and another temperature at which they increase in size.

The data of the principal runs used in determining the temperatures corresponding to points on the liquidus of each of the three crystalline phases albite, nephelite, and carnegieite are listed in Table II. In each case appropriate measures were taken to ensure that suitable crystals were present in the charges when they reached the temperature of the run. With the exception of the preparations containing 74.3, 84.2, and 91.6 per cent albite, this presented no difficulty. In these, however, the development of crystals was slow, and although we grew crystals in all these glasses in the dry way, the material

actually used to locate the liquidus at 91.6 per cent albite was prepared with the aid of sealed tubes.

The Eutectic.

The composition of the eutectic, 76 per cent albite, is given by the intersection of the liquidus of albite with that of nephelite. This intersection also gives the temperature. Inde-

TABLE III.
Eutectic temperature.

Per cent albite by weight	Temp. °C.	Time	Original condition	Condition after runs
74.3	1063	48 hrs.	Crystalline	No sign of melting
	1072	24 hrs.	Crystalline	Mostly glass
84.2	1063	48 hrs.	Crystalline	No sign of melting
	1072	24 hrs.	Crystalline	Good deal of glass

pendent evidence on the temperature was obtained by finding a temperature at which melting occurred in originally crystalline charges of the two preparations closest to the eutectic in composition, and another temperature at which it did not occur. The crystalline material was prepared in a sealed tube, and, in order that the runs at constant temperature might be as short as possible, fine-grained material was selected. The results of these runs are listed in Table III. In this case the equilibrium condition has not been approached by growing crystals, so these runs do not demonstrate that the temperature 1063°, at which no melting was obtained in 48 hours, is below the temperature of the eutectic. The judgment that it is below rests on the contrast between the product of this run at 1063° and the product of the run at 1072°. It has been placed at 1068° ± 5°.

Solids.

The solidus of a crystal species is a curve, all points on which represent the temperature and composition of crystals of the given species that can coexist in equilibrium with liquid. Thus in the equilibrium diagram, Fig. 1, the curve separating the field labelled carnegieite from that labelled carnegieite + liquid is the solidus of carnegieite. A downward extension of this curve is probably realizable in practice, but the conditions represented by it would be metastable, and the diagram represents

TABLE IV.
Solidus of carnegieite and of nephelite.

Per cent albite by weight	Temp. °C.	Time	Original condition	Condition after runs
5.2	1459	13 hrs.	Carnegieite	Carnegieite with a little interstitial glass
	1447	21 hrs.	Glass	Carnegieite. No glass found
10.9	1439	9 hrs.	Carnegieite	Carnegieite with interstitial glass
15.0	1288	15 hrs.	Glass	Carnegieite with traces of glass
15.8	1317	16 hrs.	Carnegieite	Carnegieite with glass
17.0	1288	45 hrs.	Glass	Carnegieite with glass
17.0	1268	21 hrs.	Nephelite	Nephelite + glass
	1259	23 hrs.	Nephelite	Nephelite + trace of glass in rare grains
	1250	45 hrs.	Nephelite	Nephelite. No glass found
20.0	1268	21 hrs.	Nephelite	Nephelite + glass
	1259	23 hrs.	Nephelite	Nephelite + glass
	1250	45 hrs.	Nephelite	Nephelite + glass
	1226	42 hrs.	Nephelite	Nephelite. No glass found
25.3	1200	24 hrs.	Nephelite	Nephelite + glass
			Glass	Nephelite + glass
	1160	48 hrs.	Nephelite	Nephelite
			Glass	Nephelite

only stable equilibrium. The composition of the liquid, with which the crystals can coexist in equilibrium at any temperature, is shown by a corresponding point on the liquidus.

The data used in locating the solidus of carnegieite and that of nephelite are given in Table IV. The data on the solidus of albite are in the text of the latter part of this section. As will appear from the following discussion, these curves are not located as well as the corresponding liquidus.

The experimental work to locate the solidus of carnegieite, and that of nephelite, aimed, first, at the complete crystallization of a series of homogeneous glasses to crystals of uniform composition, and then at the determination of the lowest temperature at which liquid would form from these crystals. The decision that a temperature is not above that of the solidus rests on the non-occurrence of melting at the given temperature. With very viscous materials this, by itself, would prevent the location of a point on the solidus with the same satisfaction as a point on the liquidus at the same temperature.

The preparation of completely crystalline material is frequently difficult. Indeed one rarely succeeds in *completely* crystallizing a silicate preparation. It is evident that, if the

composition of the glass is not exactly that of the crystals that separate from it, some residual liquid will remain. The failure of the glass to be of exactly the right composition may be due to any of a number of causes such as: impurities in the materials from which the glass is made, differential loss of materials in making the glass, inhomogeneity causing local departures from the correct composition, etc. Yet, when allowance is made for all possible departures of the glass from the right composition, it commonly seems as if there must be something more than this preventing the crystallization of the last interstitial liquid.

In general, then, the determination that a temperature is above that of the liquidus for a given composition involves judgment of the relative amount of glass in two preparations: the original crystallized material and the material that has been heated at the given temperature. The more completely crystallized the original material is, the more readily small increases in the amount of glass can be recognized, and, other things being equal, the closer to the solidus the temperature at which melting can be recognized.

The glasses used in the determination of points on the solidus of nephelite crystallized rapidly to a condition in which no trace of glass was visible. However, judging from the nature of the extinction, the crystallization was spherulitic, and experience with silicates has given ample reason to suspect that such material may be but partially crystallized. Complete crystallization usually results in the development of numerous voids,¹⁸ and these products were quite free from voids. Moreover, the index of refraction was low. After the material had been heated for several days, voids were plentiful, and the index of refraction was up, but it was not possible to say whether or not the material was completely crystallized to nephelite, for the index of refraction is not sufficiently sensitive to small amounts of glass or of carnegieite, and the crystallization was still fibrous with no individual crystals to be seen. When these preparations were heated at higher temperatures, glass appeared, voids disappeared, and blocky crystals of nephelite developed, all at the same temperature. We have drawn the solidus below points representing the temperature at which this change took place, and above points representing temperatures at which it did not occur.

¹⁸ Probably due to shrinkage, but in some cases possibly in part also to the concentration and separation of gas present in the original glass.

At temperatures toward that of the eutectic the above method was unsatisfactory. We crystallized glasses containing 25.3, 33.5, and 40.2 per cent albite below the eutectic temperature. The products were spherulitic, however. We then held these materials for 3 days at 1080°. No change occurred in the 25.3 per cent material, both the others were largely unchanged but locally traces of glass had developed in each of them. Doctor Posnjak kindly made comparison X-ray powder spectrograms for us, and these showed a slight but definite difference in the positions of the lines in the patterns given by the 33.5 and the 25.3 per cent materials, but no difference was observable between the patterns from the 33.5 and the 40.2 materials. This indicates that at this temperature solid solutions extend beyond 25 per cent, but does not fix the limit. We have drawn the solidus tentatively through 33 per cent at 1080°, but hope to be able to locate it more definitely.

While we were working with these mixtures we crystallized some of the glasses at 600° and Doctor Posnjak made an X-ray examination of them. The photographs agree with those made on the material described above, showing no difference in the extent of solid solution at that temperature.

The glasses used for locating the solidus of carnegieite also crystallized rapidly to a spherulitic mass, but on continued heating in the range of stability of carnegieite, solid blocky crystals of carnegieite developed, and the cooled charges consisted of an aggregate of these crystals showing the intricate twinning due to the inversion from the high-temperature isotropic form to the low-temperature birefringent form.¹⁴ When liquid is present it collects in the interstices. The longer the heating the coarser are the crystals and the better is the opportunity to see a given amount of interstitial glass. Small amounts of interstitial glass can be seen only by virtue of a difference between the refractions of the glass and the crystals. The index of refraction of carnegieite is so close to that of the glass that it would be quite impossible to see the first traces of glass developed, and this difficulty is accentuated by the twinning.

A question of considerable interest to petrology is whether or not the composition of albite can vary toward nephelite, that is, whether or not solid solutions lower in silica than albite occur in this binary system. In an attempt to answer this, glasses containing 90, 95, 97, 98, and 100 per cent of albite

¹⁴ Bowen, N. L., and Greig, J. W.: This Journal, 10, 204-212, 1925.

were prepared, then crystallized by heating in sealed tubes, followed by two months in air at about 1035° . Several preparations were made from each glass and the most favorable was selected. The crystals obtained in this way are not spherulitic, and small traces of interstitial glass are easily seen. It has already been said that it is usually difficult to crystallize a material *completely*, and these compositions are more difficult to crystallize than most that have been investigated. It was possible under the microscope to see glass in all these preparations; nevertheless they were excellently crystallized.

If it were possible to show whether or not nephelite was present in these preparations, one could, by the presence of nephelite, fix a limit to the extent of solid solution at the temperature at which crystallization took place, and by its absence, in these well-crystallized preparations, fix a composition to which solid solutions extend. However, this could not be done, either by the microscope or by the X-ray. The indices of refraction of nephelite and of albite are so nearly the same that small amounts of nephelite would not be seen in these fine-grained preparations, and Doctor Posnjak found, on comparing the spectrograms of albite and nephelite solid solutions, that the strong lines of each pattern were so nearly identical in position that it would be impossible by this means to detect a few per cent of nephelite crystals mixed with albite.

Although the expectable change in spacing accompanying a small change in the silica content of albite is very slight, Doctor Posnjak kindly made comparison X-ray powder spectrograms of these materials using molybdenum $K\alpha$ radiation. No differences were found.

The preparations were heated at 1072° - 1075° , that is, just above the eutectic temperature, for three days, after which some glass was present in the 90 and 95 per cent preparations. After a further eight days at this temperature, examination showed more glass in the 90 per cent preparation but no apparent change in the 95 per cent. No detectable change took place in the 97 or 98 per cent preparation. Other charges of the same materials were heated for fifteen days at 1079° with the same results.

The evidence leaves much to be desired, but, on the basis of these experiments, we are of the opinion that some solid solution does occur, and tentatively have placed the limit at 1075° between 95 and 97 per cent albite, i.e. at 96 per cent albite. We hope to secure further information on this point.

The Nephelite-Carnegieite Inversion.

The principal data fixing the temperature of this inversion are listed in Table V. To determine these temperatures we crystallized samples of the glasses (with the exception of the 33.5 per cent glass) completely to carnegieite and to nephelite. No difficulty was experienced in obtaining materials completely carnegieite, but we found that in the temperature region in which crystallization is fairly rapid, carnegieite formed first and that nephelite was obtained only by inverting the carnegieite. To convert the carnegieite completely to nephelite was a slow process. Instead of doing this, charges were crystallized to nephelite at low temperatures in sealed tubes. The inversion temperature, in the pure end member, was found to lie between 1259° and 1249°. Bowen¹⁵ found it to lie between 1245° and 1252°.

With increase in the silica content of the solid solutions the temperature of the inversion rises. The change does not then take place at a single temperature but over a range of temperatures, as indicated on the equilibrium diagram by the field labelled carnegieite + nephelite. The data do not well define the width of this field. Were it possible to locate the solidus curves of nephelite and of carnegieite more closely the boundaries would of course be better located.

Jadeite.

The composition of jadeite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, lies between that of nephelite and albite, but no crystals of jadeite were found in any of our preparations. The non-occurrence of crystals of this compound does not prove that it is not stable. However, if crystals of this compound decompose under these conditions, the compound is unstable, and does not enter into the equilibrium diagram. In an effort to decide this, we obtained several specimens of jadeite, and, on the basis of microscopic examination, selected one of them. This was a piece from a specimen of white jadeite from Burma, U. S. National Museum number 94303, which we obtained through the courtesy of Dr. William F. Foshag. The specimen contains good-sized crystals of jadeite mixed with a little interstitial albite. The albite was removed by using a heavy liquid.

¹⁵ Bowen, N. L.: This Journal, 33, 551-573, 1912. It may be noted in passing that whereas our materials inverted very slowly indeed, Bowen obtained almost complete conversion of nephelite to carnegieite in one hour at 1252°, and partial conversion of carnegieite to nephelite in one hour at 1245°.

TABLE V.
Nephelite-carnegieite inversion.

Per cent albite by weight	Temp. °C.	Time	Original condition	Condition after runs
0.3	1249	24 hrs.	Nephelite	Nephelite
			Carnegieite	Carnegieite
		48 hrs.	Nephelite	Nephelite
			Carnegieite	Carnegieite with a little nephelite
5.2	1268	23 hrs.	Nephelite	Carnegieite
	1259	24 hrs.	Nephelite	Nephelite
		48 hrs.	Nephelite	Nephelite + carnegieite
	1250	28 hrs.	Nephelite	Nephelite
			Carnegieite	Carnegieite + a little nephelite
	1259	48 hrs.	Nephelite	Nephelite
			Carnegieite	Carnegieite
	1269	24 hrs.	Nephelite	Nephelite
10.9	1277		Carnegieite	Carnegieite
		24 hrs.	Nephelite	Nephelite
		48 hrs.	Nephelite	Nephelite + carnegieite
	1285	4 hrs.	Nephelite	Nephelite + carnegieite
			Carnegieite	Carnegieite + rare nephelite
	1269	24 hrs.	Nephelite	Nephelite
		48 hrs.	Carnegieite	Carnegieite + increase in nephelite
	1277	24 hrs.	Nephelite	Nephelite
15.8		48 hrs.	Nephelite	Nephelite + carnegieite
	1259	48 hrs.	Nephelite	Nephelite + trace glass
	1269	24 hrs.	Carnegieite	Carnegieite + rare nephelite
		48 hrs.	Carnegieite	Carnegieite + increase in nephelite
	1273	22 hrs.	Carnegieite	Carnegieite + rare nephelite + trace glass
	1277	24 hrs.	Nephelite	Nephelite + trace glass
			Carnegieite	Carnegieite + trace glass
	1285	24 hrs.	Nephelite	Nephelite + trace glass
33.5			Nephelite	Nephelite + glass + a little carnegieite
	1268	4 hrs.	Carnegieite + glass	Carnegieite + glass + nephelite
	1273	22 hrs.	Carnegieite + glass	Carnegieite + glass + nephelite
	1285	4 hrs.	Nephelite	Nephelite + glass
		24 hrs.	Nephelite	Nephelite + carnegieite + glass

The indices of the jadeite, for which we are indebted to Dr. H. E. Merwin, follow: β 1.657, the total variation of β being less than 0.002, γ 1.668 (highest found), α 1.650 (lowest found).

The jadeite was then heated in air in an electric furnace. Decomposition was observed as low as 800° C. After having been heated at 1015° it was entirely converted to glass and large nephelite crystals. Although this jadeite is not pure

$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, its conversion to nephelite plus liquid at higher temperatures is sufficient evidence to support the conclusion that jadeite is not stable under the conditions represented by the equilibrium diagram.

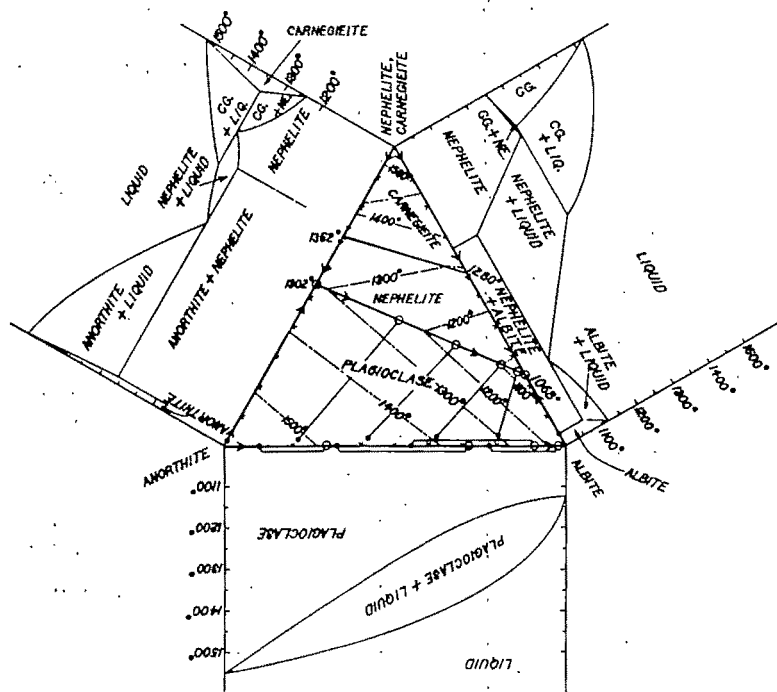


Fig. 2. The equilibrium diagrams for the systems, nephelite, carnegieite—
anorthite (Bowen, N. L.: This Journal, 33, 551-573, 1912) and the binary
system, albite—
anorthite (Bowen, N. L.: This Journal, 35, 577-599, 1913).
are combined with the diagram of Fig 1. The ternary diagram (which
is entirely hypothetical) has been drawn from these three binary diagrams,
points being located by straight line interpolation. An open circle repre-
sents the composition of a liquid that can coexist in equilibrium with crystals
of the composition indicated by that filled circle that is joined to the open
circle by a tie line.

SUMMARY.

The experimental work is summarized in the equilibrium diagram, Fig. 1. The limiting compositions of the solid solutions have not been fixed as well as we should like. It is hoped that it may be possible to obtain more information leading to a better determination of these relationships.

Although the composition of jadeite, Na₂O.Al₂O₃.4SiO₂, lies between that of nephelite and albite, it is evidently unstable under the conditions represented in the diagram. This was to be expected, for it is not known in the ordinary igneous rocks and has been considered by petrologists to be formed only at high pressures.^{16, 17}

The equilibrium diagram for this system is very similar to that for the corresponding system, nephelite, carnegieite—*anorthite*, as determined by Bowen.² In both systems the compositions of the nephelite and the carnegieite vary within limits from Na₂O.Al₂O₃.2SiO₂ toward the composition of the feldspar, *anorthite*, or albite, or, expressing this variation in composition in other words, nephelite and carnegieite take a limited amount of feldspar into solid solution. In both systems the temperature of the inversion nephelite—carnegieite rises with increased feldspar content. At the other end of each diagram, as drawn, some slight solubility of nephelite, carnegieite in the feldspar is indicated.

Bowen found that with increasing *anorthite* content the birefringence of nephelite decreased, became zero, then increased again, the crystals having become optically positive. The small size of the nephelite crystals, that grew in the nephelite—albite liquids, prevented satisfactory measurements of the indices of refraction, but the change to optically positive nephelite does not occur in this system. These nephelites are all optically negative, as are the naturally occurring examples.

In view of the similarity of these two systems it is to be expected that closely similar relationships will be found to obtain between nephelite, carnegieite and feldspar across the ternary system, nephelite, carnegieite—*albite*—*anorthite*, modified of course by the more complex nature of the equilibrium in the ternary system. With the three binary systems known, and no intermediate compounds except jadeite known or to be expected, it is a simple matter to draw up a ternary diagram that, while not correct in detail, will show the general relationships. For the convenience of the reader such a diagram has been added (Fig. 2).

In Fig. 2 the equilibrium diagrams for the systems, nephelite, carnegieite—*anorthite*,² and *albite*—*anorthite*,⁶ have been

¹⁶ See P. Eskola: The mineral facies of rocks, Norsk Geol. Tid., 6, pt. 1-20, pp. 143-194, 1920 (The metamorphic eclogite facies, p. 168, the igneous eclogite facies, p. 182).

¹⁷ Harker, A.: Metamorphism, London, 1932, p. 308.

reproduced and to them the diagram of Fig. 1 has been added. A ternary diagram has been drawn up by combining the data from these three. Positions of points within this diagram have been located by straight line interpolation. A number of tie lines have been indicated in the feldspar part of the diagram. These are lines joining the points representing the compositions of phases that can coexist in equilibrium with each other. The open circles represent liquid, the solid circles crystals. Tie lines within the diagram are of course hypothetical. It will be noted that one set of open circles lies apparently on the boundary between the fields of nephelite and of feldspar. Liquids represented by points actually on the field boundary are of course in equilibrium with both nephelite and feldspar. No tie lines have been drawn to the points representing the composition of the nephelite crystals. It may save confusion to suppose that these circles are very close to the field boundary but actually lie within the feldspar field. A thorough description of relationships of this kind has been given by Bowen¹⁸ in his paper on the system, diopside—*anorthite*—*albite*.

¹⁸ Bowen, N. L.: *This Journal*, 40, 161-185, 1915.

THE CONSTITUTION OF SOME BORIC OXIDE COMPOUNDS.

JAMES H. HIBBEN.

ABSTRACT.

The chemical constitution and spacial configuration of boric acid, sodium metaborate, and borax have been investigated by means of the Raman effect. The Raman spectra of these compounds as crystals and in aqueous solution were determined and compared with the spectra from boric oxide and borax glasses.

These results show that, although a ring structure for boric acid is not entirely excluded, in solution the more probable structure corresponds to a plane equilateral triangle, the oxygen atoms being located at the corners and the boron atom at the center. Sodium metaborate is not a linear molecule but slightly bent, and has the symmetry C_{2v} . Borax, or sodium tetraborate, appears to be a chain molecule in the crystalline state, but in solution dissociates into boric acid and sodium metaborate. The addition of hydrochloric acid to a borax solution converts all the borax to boric acid. When sodium hydroxide is added to boric acid, in solution, the acid neutralized is converted immediately to sodium metaborate. The spectrum from borax glass bears some resemblance to that of the crystalline tetraborate, but differs quite appreciably from that of boric oxide.

Boric oxide, like silica, may exist in both the crystalline and amorphous states. The boric oxides, also like silica, may combine with the alkalis to produce a variety of crystalline or amorphous compounds and solutions. Although silica has been investigated by both spectrographic and diffraction pattern methods, boric oxide, boric acid, and boric acid salts have been examined by Raman spectra methods only recently.

Silica, as is well known, does not correspond to the triatomic molecule having the formula SiO_2 , but rather exists in the crystalline and amorphous states as a tetrahedral molecule having the symmetry T_d and the effective constitution corresponding to SiO_4 . A molecule of this type should give rise to four Raman lines, of which one is polarized and corresponds to a symmetrical vibration, and three are depolarized: These four frequencies occur near $\Delta\bar{\nu}$ 500, 600, 800, and 1000-1100 $cm.^{-1}$, where $\Delta\bar{\nu}$ represents the difference between the frequency of the Raman line and the exciting radiation expressed in wave numbers per centimeter. Actually, some of these frequency shifts are broken up into more than one component, probably because of a lack of completely regular tetrahedral symmetry.

With the boric oxide compounds the situation is quite different. Here it is possible to have a molecule of the type ABA representing the metaborate ion, which in the linear form would have the symmetry $C_{\infty h}$ and give rise to but a single Raman line. On the other hand, the molecule may be bent, in which case the symmetry would be C_{2v} and there should appear three Raman frequencies corresponding to the ν_π , ν_σ , and δ_π types of oscillation. For boric acid the most probable arrangement would be a molecule of the type AB_3 having the symmetry D_{3h} in which a "three B groups would lie at the corners of a plane triangle with the A atom in the center. This is similar to the arrangement of the NO_3 group in the nitrate ion and the CO_3 group in the carbonate ion. This configuration would give rise to three Raman lines, two of which would be doubly degenerate, and one would correspond to the symmetrical expansion and contraction of the molecule.

Recently, Ananthakrishnan¹ observed for boric acid in solution only one line at $855(3)$,² and for the crystalline H_3BO_3 two additional frequencies near $3180(3)$ and $3256(1)$. In the crystalline boric acid, Nielsen³ has observed other frequencies, $\Delta\bar{\nu}$ 503 (4), 1065 (0), and 1155 (0). Of these frequencies, those in the 3000-3600 region are connected solely with the $O \leftrightarrow H$ oscillation. These results, together with the new observations of the writer and all other Raman spectra data on boric acid and its derivatives, are shown in the table.

Ananthakrishnan attempts to correlate the largest pair of frequencies observed by him with a "hydroxyl bond" in contradistinction to a "hydrogen bond." The evidence for this distinction is not well founded, first, because the O-H frequency is present, presumably in acids supposed to exhibit hydrogen bonding, and second, because the diminishing of the O-H frequency in the alkali hydroxides from $\Delta\bar{\nu}$ 3600 to 3300, or less, does not seem to be significant of any hydroxyl bonding. The same reduction in the typical O-H shift occurs in most crystal hydrates.

In addition to the intense line at $\Delta\bar{\nu}$ 875 in an aqueous solution of boric acid, Hibben⁴ has observed also two other lines of fair intensity at $\Delta\bar{\nu}$ 506(2) and 1420(1). These two fre-

¹ Ananthakrishnan, R.: Proc. Indian Acad. Sci., 5, 285, 1937.

² Any whole digit in parenthesis following a number represents the relative intensity of this line on the basis of ten.

³ Nielsen, J. Rud: Personal communication.

⁴ Hibben, J. H.: Reported in this communication.

quencies are broad and diffuse. There occur, furthermore, two lines—or possibly one band—at $\Delta\bar{\nu}$ 1060 and 1130. If this were a single band the intensity center would be near $\Delta\bar{\nu}$ 1100. These two bands (or band) are exceedingly weak and probably correspond to the equivalent frequencies seen in the crystals, where they appear as reasonably sharp lines, although with intensities that are very feeble.

It is to be noted, therefore, that the spectrum obtained from boric acid solutions is approximately identical with that observed in the crystals with the exception of the line attributable to the O-H oscillations which are naturally masked in aqueous solutions by the O-H vibrations of the water molecule. From this similarity one may reasonably draw the conclusion that boric acid in solution contains the O-H group attached to the boron atom and that there is no possibility of the existence of a molecule having the form H_3BO_3 . This is substantiated further by the lack of any B-H line corresponding to the P-H line found in H_3PO_3 . There exist, then, three frequencies for boric acid which are beyond dispute, namely, $\Delta\bar{\nu}$ 506, 873, and 1420. This last frequency shift differs too widely from a combination of $\Delta\bar{\nu}$ 873 with 506 to be a combination frequency. The relative grouping and intensity of these three lines are reminiscent of the three Raman shifts at $\Delta\bar{\nu}$ 710, 1050, and 1340 observed in the nitrate ion.

Consider next the simplest salt of boric acid, sodium metaborate. In solution this was originally supposed to yield 253(1) and 1403(4) by Ghosh and Das,⁵ while Nielsen and Ward⁶ reported $\Delta\bar{\nu}$ 749. More recently, Nielsen³ has observed an additional line at $\Delta\bar{\nu}$ 950(1). Hibben⁴ also finds $\Delta\bar{\nu}$ 747(6), but in addition, the broad band extending from $\Delta\bar{\nu}$ 1132 to 1276 which may be made up of two separate diffused lines. The band reported from $\Delta\bar{\nu}$ 400 to 500 in the table is undoubtedly the hindered rotational band observed in water. Crystalline sodium metaborate tetrahydrate, according to Nielsen,³ yields $\Delta\bar{\nu}$ 741(5) and two frequencies at $\Delta\bar{\nu}$ 3190(1) and 3555(1). These last two frequencies are connected with the hydroxyl group in the hydrated crystals, while no other frequencies were observed between $\Delta\bar{\nu}$ 741 and 3190. They are probably in existence, but are too difficult to discern when small crystals are used.

⁵ Ghosh, J. C., and Das, S. K.: *J. Phys. Chem.*, 36, 586, 1932.

⁶ Nielsen, J. Rud., and Ward, N. E.: *J. Chem. Phys.*, 5, 201, 1937.

TABLE I.
Raman Spectra of Some Boric Oxide Compounds.

<i>Substance</i>	<i>Raman shifts</i>
1. B(OH) ₃ (Cryst.)	503(4)
2. B(OH) ₃ (Sol.)	506(2)
3. NaBO ₂ (Sol.)	253(1)
4. NaBO ₂ (Sol.)	400-500
5. Na ₂ B ₂ O ₄ (Sol.)	747(6)
6. Na ₂ B ₂ O ₄ ·4H ₂ O	743(5)
7. Na ₂ B ₂ O ₄ ·4H ₂ O	741(5)
8. Na ₂ B ₂ O ₄ ·10H ₂ O	735(3)
9. (NH ₄) ₂ B ₄ O ₇ (Cryst.)	850(0)
10. Na ₂ B ₄ O ₇ (Sol.)	853(1)
11. H ₂ BO ₃ + NaOH, 4:1	934(6)
12. H ₂ BO ₃ + NaOH, 2:1	942(1)
13. H ₂ BO ₃ + NaOH, 1¼:1	891(1)
14. H ₂ BO ₃ + NaOH, 1:2	875(6)
15. H ₂ BO ₃ + NaOH, 1:3	875(6)
16. Na ₂ B ₄ O ₇ + 4HCl	875(4)
17. Na ₂ B ₄ O ₇ (Glass)	875(3)
18. B ₂ O ₃ (Glass)	949(0)
19. B ₂ O ₃ (Glass)	873(10)
20. BO ₂ (Ion)	950-1000(0)
	803(8)
	806(5)
	602(1)
	700
	915

TABLE I (continued).

Substance	Raman shifts	References
1. B(OH) ₃ (Cryst.)	1065(0) 1155(0)	1, 3
2. B(OH) ₃ (Sol.)	1060(0) 1130(0)	1, 4
3. NaBO ₂ (Sol.)	1420(1) 1403(4)	5
4. NaBO ₂ (Sol.)	1132(0) 1276(0)	4
5. Na ₂ B ₂ O ₄ (Sol.)		3, 6
6. Na ₂ B ₂ O ₄ ·4H ₂ O	3190(1)	3
7. Na ₂ B ₂ O ₄ ·4H ₂ O	1100?	4
8. Na ₂ B ₂ O ₄ ·10H ₂ O	3269(2) 3343(3) 3425(2) 3552(10) 3340(1) 3455(1) 3574(1)	3
9. (NH ₄) ₂ B ₂ O ₇ (Cryst.)	1100(2)	7
10. Na ₂ B ₂ O ₇ (Sol.)	1132(0) 1161(0)	4
11. H ₂ BO ₃ + NaOH, 4:1	1060(0) 1132(0)	4
12. H ₂ BO ₃ + NaOH, 2:1		4
13. H ₂ BO ₃ + NaOH, 1¼:1		4
14. H ₂ BO ₃ + NaOH, 1:2	1150(0) 1220(0)	4
15. H ₂ BO ₃ + NaOH, 1:3	1160(0) 1219(0)	4
16. Na ₂ B ₂ O ₇ + 4HCl	1420(0)	4
17. Na ₂ B ₂ O ₇ (Glass)	1077-1127(0) 1310-1520(0)	10
18. B ₂ O ₃ (Glass)	1261(0)	3594(1) ? 4983(1) ? 8
19. B ₂ O ₃ (Glass)	1030(1) 1120(1) 1257(0)	9, 10, 11
20. BO ₂ (Ion)	1445	8

The principal and probably the symmetrical vibration, therefore, of the metaborate ions occurs at $\Delta\tilde{\nu}$ 747. This is present not only in solution but also in crystals, although in the latter it is reduced by a few wave numbers. This same frequency also occurs in sodium tetraborate, whose spectrum will be discussed shortly. It is obvious that the spectrum of sodium metaborate differs widely from that observed in boric acid. It was supposed originally that the BO_2 ion represented a linear grouping of a molecule of the type ABA. The appearance of additional Raman lines, however, would make this an impossibility for the reasons already mentioned in discussing molecules having the symmetry C_{2v} and a bent structure. An example of this type of molecule is SO_2 , which shows three principal Raman lines at $\Delta\tilde{\nu}$ 525, 1144, and 1334, of which the middle frequency is the most intense. Zachariassen, from X-ray measurements, has concluded that the anhydrous metaborate exists in a ring formation somewhat similar to the benzene ring with alternating boron and oxygen atoms. If this structure persisted in solution it would exist as a B_3O_6 ion. The principal objection to such an hypothesis is a dearth of Raman lines. Such a structure could have twenty-one possible different frequency shifts. The symmetry conditions would undoubtedly reduce this number by a considerable amount, but it seems probable in this case that the number would exceed one or two Raman lines.

In the spectra observed from sodium tetraborate (borax), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Nielsen⁸ has found about four lines of equal intensity, in addition to the group of three attributable to the water molecule in the crystal hydrate. Hibben⁴ likewise has observed a group of similar lines in kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, with the exception of $\Delta\tilde{\nu}$ 891 and inclusive of a strong line at $\Delta\tilde{\nu}$ 735 which was not noted by Nielsen. This shift is slightly reduced from the value near $\Delta\tilde{\nu}$ 747 in the solution of sodium tetraborate. Curiously enough, this shift was reported by Joglekar and Thatte⁷ for ammonium tetraborate in the crystalline form at $\Delta\tilde{\nu}$ 714. At the same time, however, no shift was noted by them at $\Delta\tilde{\nu}$ 934. From the intensity observed for this line it apparently is the type of vibration equivalent to that which occurs near $\Delta\tilde{\nu}$ 875 but is displaced to a higher frequency in the crystals. The spectrum obtained from the saturated solution agrees fairly well with that observed in the crystals

⁷ Joglekar, M. S., and Thatte, V. N.: *Z. Physik*, 98, 692, 1936.

with the exception of the possible splitting of $\Delta\tilde{\nu}$ 875 into several components. There is also a weak band which may be made up of a pair of lines near $\Delta\tilde{\nu}$ 1000 and 1130. The actual magnitude of these shifts can be only estimated, as these bands are too feeble and too diffused to measure with accuracy.

The question may be raised why such a strong pair of lines at $\Delta\tilde{\nu}$ 747 and 875 should appear from an aqueous solution of sodium tetraborate when the metaborate possesses only one

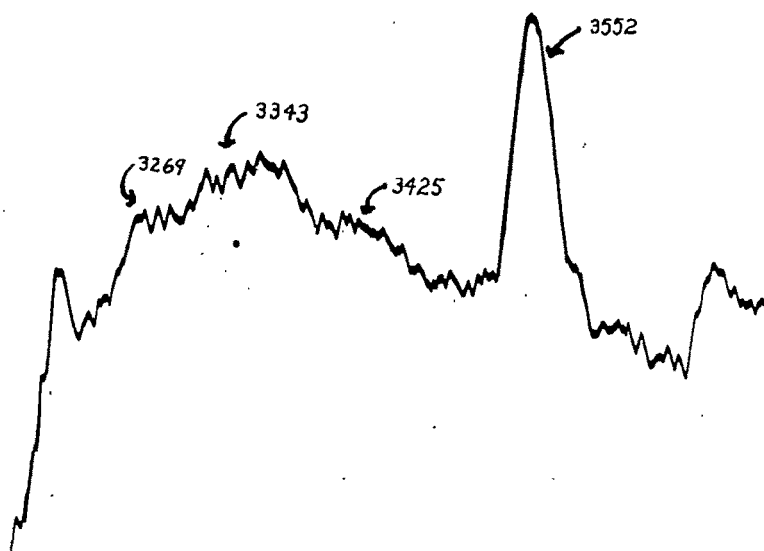


Fig. 1. Microphotometer tracing of the spectrum of O-H bands in $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$.

strong line, and boric acid similarly has only one. Furthermore, the second strong line in the tetraborate coincides with that observed from boric acid. In fact, the entire spectrum of sodium tetraborate resembles, or is identical with, the combined spectrum of boric acid and sodium metaborate. Another peculiarity is the extreme intensity of the line at $\Delta\tilde{\nu}$ 3552 in the tetrahydrate. This line is much stronger than the usual lines that may be attributed to water of crystallization, and appears near the observed shift for the OH group in boric acid. This would seem to indicate the possibility of an actual hydroxyl group of constitution being present in the crystalline

tetraborate. This is shown in the microphotometer tracing in Fig. 1.

In an attempt to throw some light on this subject, Hibben⁴ initiated a series of studies of solutions of boric acid containing variable amounts of sodium hydroxide. The results of these experiments are indicated in Figs. 2 and 3, which show not

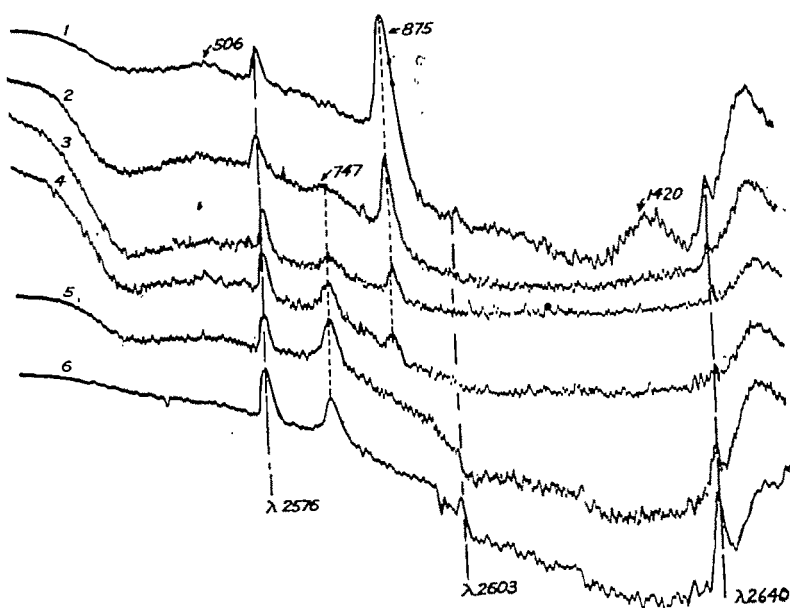


Fig. 2. Microphotometer tracings of the Raman spectra obtained from a solution of boric acid containing varying amounts of sodium hydroxide. Curve 1 represents the spectrum from a solution of pure boric acid; curves 2 to 6 are from a 0.18 molal boric acid solution to which has been added sodium hydroxide to yield the following ratios of boric acid to sodium hydroxide respectively: 4:1; 2:1; $1\frac{1}{4}$:1; 1:2; 1:3.

only the effect of the addition of sodium hydroxide to boric acid, but also give a comparison spectrum of the crystalline tetraborate and metaborate. In Fig. 2, line one represents the spectrum of aqueous boric acid solution. This microphotometer tracing shows the three strongest lines. The weakest ones were too feeble to register on the microphotometer but are visible on the original plates. The addition of a small quantity of sodium hydroxide to these solutions immediately produces a

broad band whose maximum is at $\Delta\bar{\nu}$ 747 and a diminution in intensity of $\Delta\bar{\nu}$ 875. As sodium hydroxide is added, the $\Delta\bar{\nu}$ 875 progressively decreases and the 747 becomes less broad and increases in intensity. When the ratio of the boric acid mole-

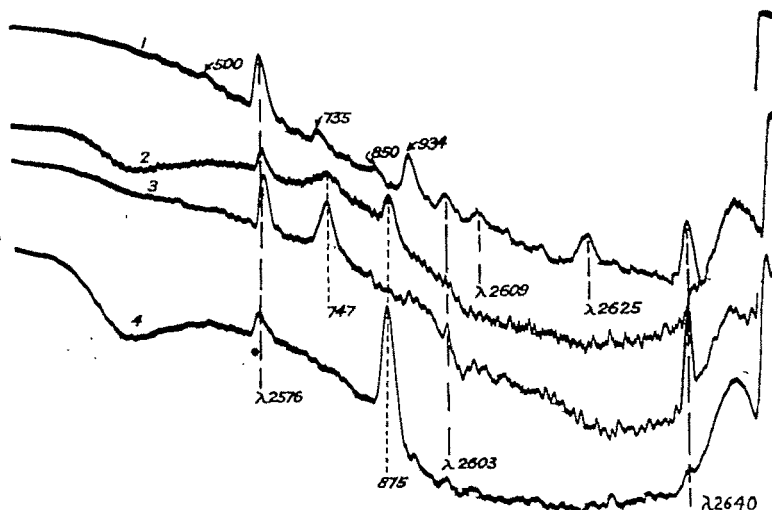
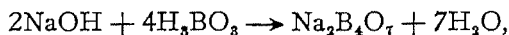
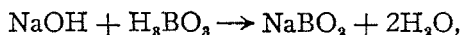


Fig. 3. Microphotometer tracings of the Raman spectra obtained from some salts of boric acid. Curve 1 represents the spectrum from $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$; curve 2 is from an aqueous solution of sodium tetraborate; curve 3 is from an aqueous solution of sodium metaborate; and curve 4 is from an aqueous solution of sodium tetraborate to which has been added a molecular excess of hydrochloric acid.

cules to sodium hydroxide molecules has the value of 2:1, or sufficient sodium hydroxide is added to convert all the boric acid to sodium tetraborate, according to the equation,



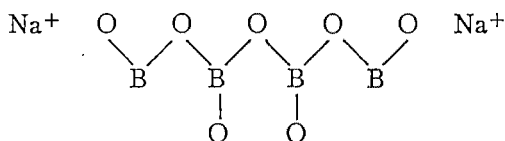
then the intensities of these two lines are nearly equal, giving a spectrum which is comparable with that observed for the tetraborate. When the molecular ratios are 1:1, and sodium hydroxide has been added to form NaBO_2 , according to the equation,



the line at $\Delta\bar{\nu}$ 875 completely disappears. The addition of greater quantities of sodium hydroxide causes no further change in the principal line of the spectrum. The addition of an excess quantity of hydrochloric acid to a solution of sodium tetraborate causes the disappearance of $\Delta\bar{\nu}$ 747, as shown in Fig. 3, and the strengthening of 875, or in short, the reversion to boric acid.

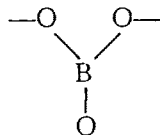
These results are best explained on the assumption that sodium metaborate, NaBO_2 , is produced initially by the addition of sodium hydroxide to boric acid. Consequently there is a mixture of boric acid and the metaborate always present until one molecule of the base has been added for each molecule of the acid, at which time the conversion is complete. When sodium tetraborate is dissolved in water, it dissociates into $2\text{NaBO}_2 + 2\text{B}(\text{OH})_3$, where the NaBO_2 is ionized into Na^+ and BO_2^- ions. According to this conception, the tetraborate is completely, or nearly completely dissociated in solution.

If the crystalline sodium tetraborate has the following chain formation:

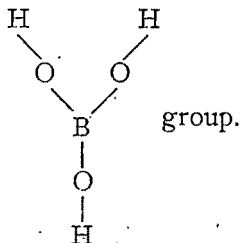


then the two end $\left[\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{B} \end{array} \right]^-$ groups would have a vibration sim-

ilar to sodium metaborate, and the intermediate



groups should have a vibration resembling the



M. K. Sen and A. K. Sen Gupta have investigated the infra-red absorption spectra of the borates of lithium, potassium, calcium, magnesium, copper, and lead. These authors conclude that the borate ion has a plane configuration and somewhat resembles that of the NO_3 and CO_3 ions. It is presumed from this analogy that they refer to the existence of a BO_3 ion. The origin of a BO_3 ion from the $\text{R}_2\text{B}_4\text{O}_7$ is not entirely clear. The nearest approach is the BO_3 group in the chain of the crystalline tetraborate as indicated above. The absorption frequencies observed by them in the infra-red correspond to $\Delta\tilde{\nu}$ 709, 917, and 1315. The fourth frequency calculated by them to be the inactive vibration, so far as infra-red absorption is concerned, would fall at $\Delta\tilde{\nu}$ 1111. This vibration should correspond to the ν_1 type of oscillation or the symmetrical polarized frequency which appears most strongly in the Raman effect. This is obviously at $\Delta\tilde{\nu}$ 934, and it is difficult to correlate this result with the calculated $\Delta\tilde{\nu}$ 1111.

On taking up next the question of boric oxide as found in boric oxide glass, it can be seen that the observations of different observers are none too concordant. In the table referred to, item 18 gives the observations of Langenberg.⁸ Item 19 includes the results of Avramenko,⁹ Gross and Vuks,¹⁰ and Kujumzelis.¹¹ Of these frequency shifts, only $\Delta\tilde{\nu}$ 806 and 1260 were obtained by all the workers. Gross and Vuks record $\Delta\tilde{\nu}$ 1120 while Avramenko adds $\Delta\tilde{\nu}$ 602 and 1030. The only lines which may be ascribed to boric oxide with absolute certainty are, therefore, $\Delta\tilde{\nu}$ 806 and 1260. Item 20 refers to what Langenberg is pleased to call the BO_3 ion in glasses.

From the standpoint of infra-red absorption, one may consider, then, that there are two bands which have their counterpart in the Raman effect near $\Delta\tilde{\nu}$ 700 and 915, but that $\Delta\tilde{\nu}$ 1315, observed in infra-red, has no shift in the Raman effect near this region except 1261 or 1445. So far as considering a BO_3 group in B_2O_3 as analogous to the NO_3 one, it should be pointed out that boric acid possesses the nearest known counterpart to a BO_3 group, and that this acid has no Raman lines which correspond to those observed from the boric oxide glass.

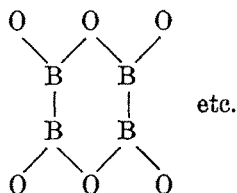
⁸ Langenberg, R.: *Ann. Physik*, 28, 104, 1937.

⁹ Avramenko, E. I.: *J. Phys. Chem. (U. S. S. R.)*, 7, 339, 1936.

¹⁰ Gross, von E., and Vuks, M.: *Compt. rend. acad. sci. U. S. S. R.*, 1, 214, 1935.

¹¹ Kujumzelis, G.: *Z. Physik*, 100, 221, 1936.

Of course, several formulas may be set up to depict the structure of B_2O_3 . Among these is the following:



This has the objection, already raised, of probably yielding a Raman spectrum more complicated than the one observed. Other structures such as an asymmetric tetrahedron similar to that of phosphorus oxychloride would give rise to six Raman lines, while a linear one of the type A-B-A-B-A would yield but three frequency shifts. In the absence of polarization and accurate intensity data, it is impossible to assign accurately any specific structural configuration for boric oxide in boric oxide glass from the Raman spectra information. It can be shown, nevertheless, that a number of possible configurations are improbable.

In borax glass there is observed by Gross and Vuks¹⁰ a diffuse band from $\Delta\bar{\nu}$ 430-535, a very strong line at $\Delta\bar{\nu}$ 760, and three bands extending from 950-1000, 1077-1127, and 1310-1520. The maxima of these lines are in reasonable agreement with the results obtained from the crystalline sodium tetraborate, with the possible exception of the frequency at $\Delta\bar{\nu}$ 934 which is much stronger than the one reported by Gross and Vuks for the same displacement. The lack of a frequency equivalent to $\Delta\bar{\nu}$ 875 as observed in solutions of boric acid containing sodium hydroxide, and the closer approach to the crystalline results, would apparently indicate a nearer relationship of the glass to crystalline borax than to the products formed in an aqueous solution of sodium tetraborate.

SUMMARY.

The results of these investigations indicate that boric acid is a molecule of the type AB_3 having the symmetry D_{3h} in which all the B groups lie at the corners of a plane triangle with the boron atom in the center. Crystalline boric acid has a spectrum which shows the presence of O-H linkages and the complete absence of any B-H linkage.

It had been supposed previously that the BO_2 ion in sodium metaborate corresponded to a linear group of the type A-B-A which would result in the appearance of only one Raman line. Since at least two lines have been observed, it would seem reasonable to conclude that the ion has a bent structure with the symmetry C_{2v} . There are no lines present in the solution of this compound which would correspond to a $\text{Na} \leftrightarrow \text{B}$ vibration, thus indicating complete ionization. Proposed structures of this molecule, based on a polymerized model or on a configuration resembling a benzene ring, are rejected on the ground that the simplicity of the Raman spectrum is not in accord with such an interpretation.

The spectrum from sodium tetraborate indicates a dissociation of this compound into sodium metaborate and boric acid on solution. The addition of sodium hydroxide to boric acid apparently produces sodium metaborate in equilibrium with boric acid, and there is no compound comparable to crystalline sodium tetraborate in an aqueous solution. The addition of hydrochloric acid to a solution of sodium tetraborate results in the formation of boric acid. The stepwise conversion of boric acid to sodium metaborate in equilibrium with boric acid or the complete conversion to the metaborate, is demonstrable by means of Raman spectra.

The spectrum of crystalline sodium tetraborate indicates that it is apparently nearly a composite of the spectra obtainable from BO_2 ions and from BO_3 groups. This is reasonably consistent with the supposition that sodium tetraborate is made up of long chains both in the crystalline and amorphous forms.

Several formulae have been proposed to depict the structure of B_2O_3 in glasses. From the data at hand it is not possible to designate which of the structures is correct, but it is possible to indicate that some of them are incorrect.

ALBITE TRENDS IN SOME ROCKS OF THE PIEDMONT.

EARL INGERSON.

ABSTRACT.

There are albite porphyroblasts in most of the rocks of the Piedmont province of southern Pennsylvania and northern Maryland. Many of these albite metacrysts show "trends," that is, they have inclusions that show pronounced alignments. These trends have been interpreted as relict structures indicative of older periods of metamorphism. The present work shows that the albite trends in the Port Deposit granodiorite complex and associated rocks are not relict structures, but are controlled by the lattice of the feldspar grains. They were probably developed by late hydrothermal activity. This does not mean that there has been only one period of metamorphism affecting these rocks, but merely that the albite trends cannot be used as evidence for other periods of metamorphism. Similar studies from the literature are cited. In some of these, the trends appear to be true relict structures. In others, they are related solely to the lattice of the host feldspars.

INTRODUCTION.

In many tectonites, late porphyroblasts contain inclusions of other minerals. Sander¹ has outlined the theoretically possible relations that the orientation of these inclusions may show to that of the same minerals of the "groundmass."² These possibilities may be grouped under three heads:

1. The included minerals may show random orientation.
2. They may have the same preferred orientation as the same minerals of the groundmass.
3. They may have a preferred orientation that is different from the fabric of the groundmass.

Most of the rocks of the Piedmont of southern Pennsylvania and northern Maryland contain porphyroblasts that have other minerals included in them. Of these, albite is the most wide-

¹ Sander, B.: Über Tektonite mit Gürtelgefüge, Fennia, 50, No. 14, 1-25, 1928.

² The term "groundmass" is used for convenience and brevity to indicate the part of the rock outside of the porphyroblasts, whether the rock was originally of igneous or sedimentary origin.

spread, although there are also porphyroblasts of muscovite, biotite, tourmaline, and garnet. The albite porphyroblasts occur in all the rocks of Ordovician age and older, being present, for example, in the Conestoga limestone, Vintage dolomite, Antietam quartzite, Peters Creek schist, Wissahickon and Baltimore gneisses, the Port Deposit granodiorite complex, and even in the gabbroic intrusions. In general, the albite in the schists and gneisses has formed by replacement of quartz, mica, and other minerals, whereas that in the igneous rocks has formed at the expense of more calcic plagioclase.

Commonly, the inclusions in the albite porphyroblasts are arranged in more or less well-defined "trends"; that is, the inclusions of quartz, mica, epidote, garnet, and other minerals show definite alignments, which may be either straight or curved.

It can be seen at a glance that the minerals of these trends, especially the micas, have a strong preferred orientation that is different from that of the groundmass (Fig. 10). Therefore, of the possible relations, only case (3) need be considered for these albite trends. Of the several possible origins of an "internal fabric" (Ri) different from that of the groundmass (Re), there are three that should be considered in a study of the Piedmont rocks:

(a) The inclusions may be parts of an older fabric that have been preserved by the protective action of the albite porphyroblasts during the development of a different orientation in the groundmass.

(b) They may be included portions of the existing fabric of the groundmass that have been turned out of position by rotation of the porphyroblasts.

(c) The orientation of the inclusions may be related to the lattice of the individual feldspar crystals and neither to the present nor to an older fabric of the rock as a whole.

PREVIOUS INTERPRETATIONS.

These albite trends in rocks of the Piedmont have been interpreted exclusively as relict structures, but different writers have different ideas as to how they originated. Knopf and Jonas⁸ describe trends in the Wissahickon that are straight and regular, but show an angular discordance with the struc-

⁸ Knopf, E. B., and Jonas, A. I.: *Geology of the McCall's Ferry-Quarryville District of Pennsylvania*, U. S. Geol. Survey Bull., 799, 29-30, 1929.

tures in the groundmass. This angular discordance is taken as evidence of a rotation of the metacrysts, which involves the assumption that the included minerals are older than the albite porphyroblasts.

There are all gradations between these straight trends and the crumpled ones described by Singewald.⁴ A moderately curved trend from the Antietam is pictured by Cloos.⁵ Singewald pictures trends from the Wissahickon that are slightly crumpled and appear to be approximately parallel to the mica of the groundmass⁶ and also trends that are badly crumpled and whose mica flakes appear to stand at a high angle to those of the groundmass.⁷ Singewald accepts the relict interpretation for these trends, but doubts that rotation has been effective. He believes that the folding of the mica flakes took place before the development of the porphyroblasts and that the apparent angular discordance can be explained by fortuitous development of the metacrysts without any rotation.⁸

STATISTICAL STUDY.

These albite trends are most striking where mica is the included mineral, but many consist of other minerals such as quartz, epidote, or garnet. These trends of other minerals are more difficult to study quantitatively, but where they are present in the same feldspar grain with mica they appear to be parallel to the mica and presumably have the same origin and significance.

I have been unable to find a published suggestion that any of these albite trends in Piedmont rocks may be related to the lattice of the feldspar. However, when I began to study thin sections of the Port Deposit complex and surrounding rocks, I was impressed by the regularity of the albite trends—they are much more regular than the mica orientation in the

⁴ Singewald, J. T., Jr.: Weathering and albitization of the Wissahickon schist at the Prettyboy dam, Baltimore County, Maryland, *Bull. Geol. Soc. Am.*, 43, 449-468, 1932.

⁵ Cloos, E.: The application of recent structural methods in the interpretation of the crystalline rocks of Maryland, *Maryland Geol. Survey*, 13, Pl. 9, 1937.

⁶ *Op. cit.*, Fig. 3.

⁷ *Op. cit.*, Fig. 4.

⁸ *Op. cit.*, p. 461.

groundmass—and it occurred to me that the arrangement might be parallel to important lattice planes of the feldspar grains, even when they show no cleavage. Figures 2, 5, and

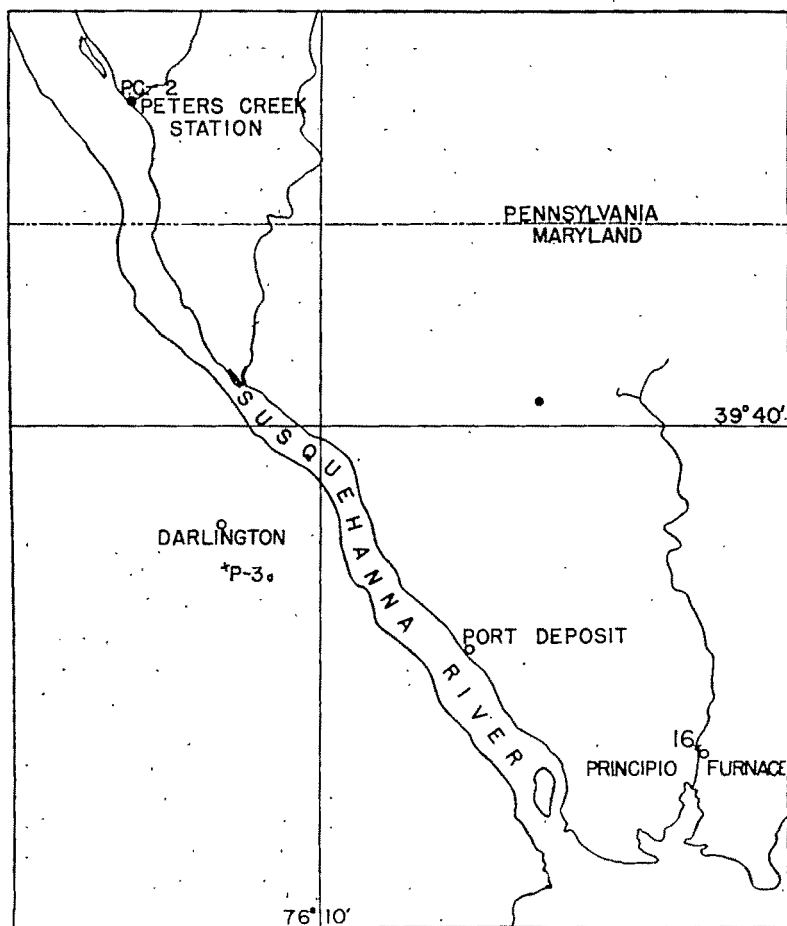


Fig. 1. Index map showing where the specimens whose trends have been analyzed were collected.

10 are photomicrographs of albite porphyroblasts each of which shows one or more trends.

It was a simple matter to test this hypothesis of crystallographic control by making a statistical study of the orientations of all the inclusions in a given albite crystal, and then plotting



Fig. 2. Photomicrograph of an albite porphyroblast from the granitic facies of the Port Deposit granodiorite at Principio Furnace. Thin section 16. Notice the straightness of the "trends," which are, in this case, included muscovite flakes. Crossed nicols. x 65.

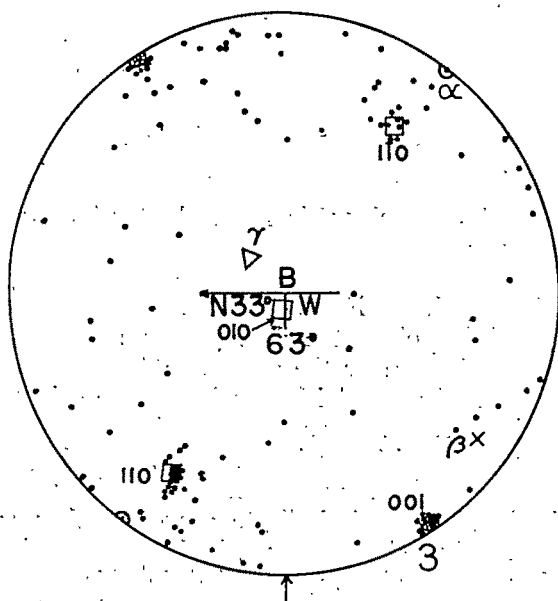


Fig. 3. Equal area projection of the important elements of the crystal shown in Fig. 2 and of the poles of its included mica flakes.

on the same diagram the orientation of the host porphyroblast. These statistical studies were made by plotting the poles of the mica inclusions on an equal area net. The manner of projection is exactly the same as in stereographic projection except that the lower hemisphere is represented rather than the upper one. On the universal stage we can measure the angle that the trace of a cleavage plane makes with the horizontal cross hair, and the angle in space that the plane of the cleavage makes

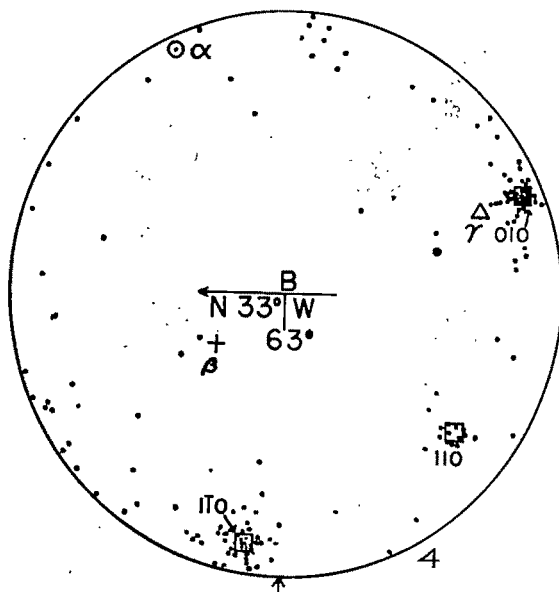


Fig. 4. Projection of another albite porphyroblast and its included mica; from thin section 16.

with the thin section. From these two angles we can plot the position of the pole to the cleavage plane.

Plotting in this manner the poles of all the mica flakes in a given porphyroblast establishes definitely the orientations of the planes of the trends. By suitable manipulations, the optical indicatrix and the positions of the important lattice planes for the same porphyroblast can be measured and plotted on the same projection, which will indicate clearly whether or not the trends lie parallel to cleavage or twinning planes of the host.

A number of trends were studied in this manner, and Fig. 1 indicates where the specimens were collected. Most of the diagrams thus far prepared have been made from specimen

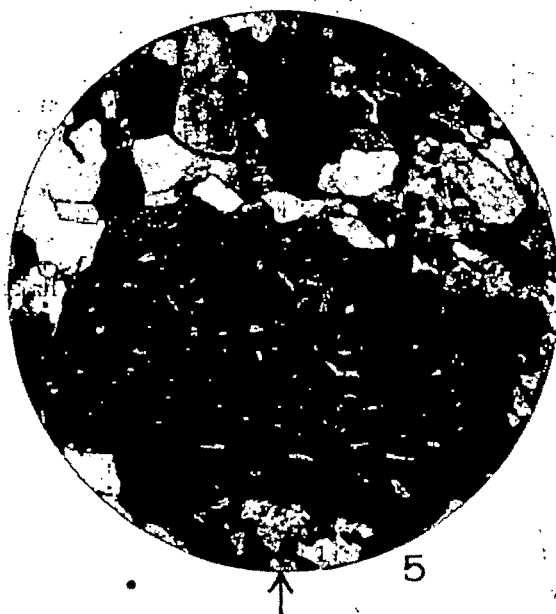


Fig. 5. Photomicrograph of another albite metacryst from thin section 16. Crossed nicols. $\times 65$.

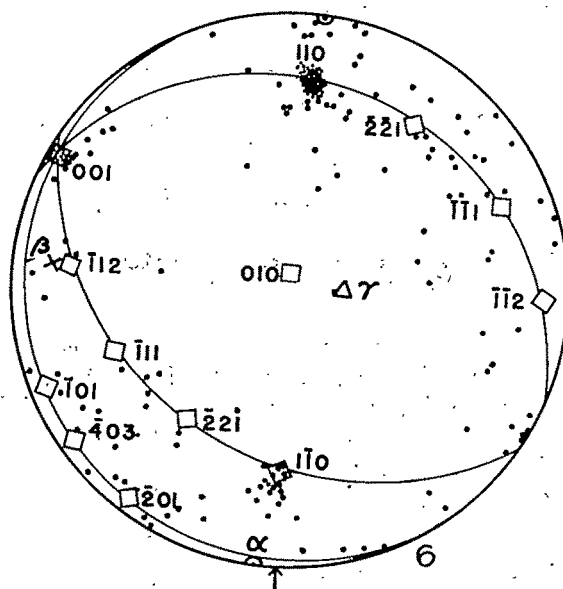


Fig. 6. Projection of the albite crystal shown in Fig. 5, with the important crystallographic zones shown. Note that all the poles of the included mica flakes fall in, or near, these zones.

16, collected from a granitic facies of the Port Deposit complex at Principio Furnace, Maryland. Specimen P. C.-2 is from the Peters Creek schist at Peters Creek station, Pennsylvania, and P.-3a is from a granite streamer in gneiss south-east of Darlington, Maryland.

Figure 2 is a photomicrograph of a porphyroblast from specimen 16. Fig. 3 is a projection of the important elements of this crystal, and of the poles of the mica flakes that it

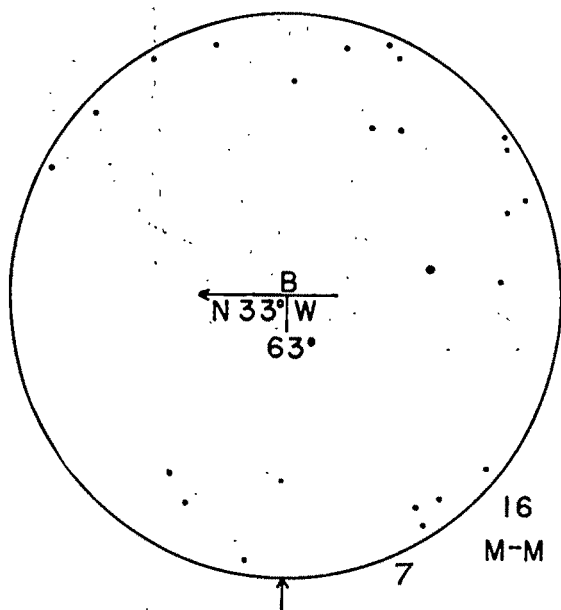


Fig. 7. Poles of twenty-three feldspar lattice planes that control trends of mica inclusions. All are from thin section 16.

includes. There are strong maxima of the poles of the mica flakes corresponding exactly to the (001), (110), and ($1\bar{1}0$) planes of the feldspar, indicating a definite control of the orientation of the inclusions by the lattice of the feldspar. In each example the orientation of the photomicrograph of a crystal and that of its projection are the same, so that the trends in the pictures can be readily correlated with the maxima of the diagrams.

Figure 4 is a similar projection of another albite porphyroblast from the same thin section. It shows strong maxima in (010), (110), and ($1\bar{1}0$) of the feldspar. In each of these

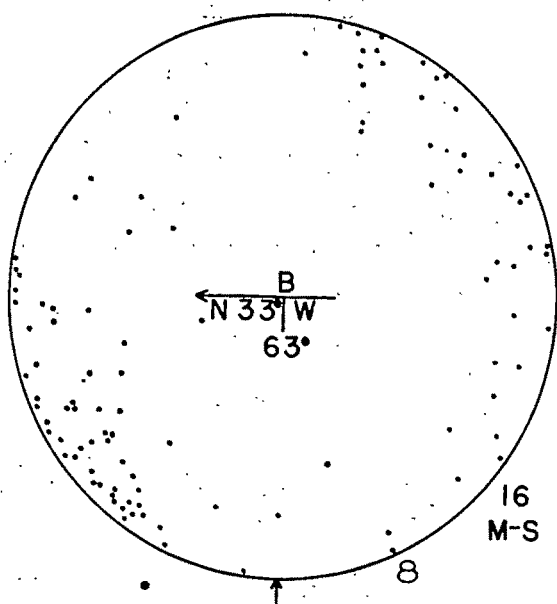


Fig. 8. Poles of 104 mica flakes lying in the s -planes of the groundmass of thin section 16.

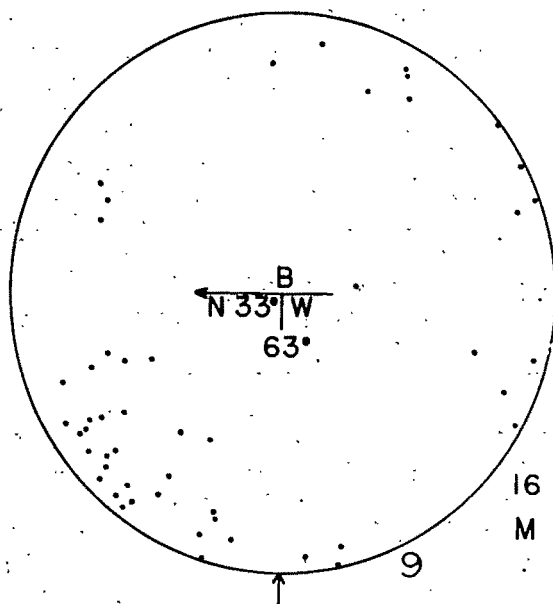


Fig. 9. Poles of 50 mica flakes lying between the s -planes of the groundmass of thin section 16.

projections there are a number of points that do not coincide with the poles of any of the cleavage planes. These are the mica flakes that do not lie in the definite trends. These flakes may (1) show random orientation, (2) be related to the fabric of the groundmass, or (3) be controlled by subordinate planes of the feldspar lattice.

Figure 5 is a photomicrograph of still another albite crystal from specimen 16, and Fig. 6 is a projection of this porphyroblast and the poles of its included muscovite plates. The mica flakes are mostly controlled by (001), (110), and (1 $\bar{1}$ 0). The zones containing these planes have been indicated on the projection and it is evident that *all* the mica flakes lie in or near these zones. This fact suggests that all the mica flakes may be controlled by the lattice of the feldspar, but it is by no means conclusive evidence. The surely established fact is that *the trends are controlled by the important lattice planes of the feldspar*.

Twenty-three such trends were measured from thin section 16, and Fig. 7 is a projection showing their positions. Each point is the pole of a feldspar plane that determines the position of a trend.

In order to see whether there was any relation between these trends and the fabric of the groundmass, diagrams of the muscovite fabric of the groundmass were prepared.

Figure 8 is from the muscovite of the groundmass in the *s*-planes, and Fig. 9 is from the muscovite of the groundmass between the *s*-planes. The maxima of the two diagrams coincide, indicating that the mica fabric of the groundmass is homogeneous. They do not correlate with the maxima from the diagrams of individual feldspar crystals and their inclusions, Fig. 7, except that in both cases the poles tend to form a girdle about the fold axis (= *B*-axis of the fabric), which is the center of each projection.

This indicates an indirect relation of the albite trends to the fabric of the rock in this way—the cleavage planes of each albite grain that were in the zone of the *s*-planes of the rock (i.e. parallel to the axis of folding, or rotation), were the ones that were developed and along which the inclusions grew.

The diagrams from the other specimens show practically the same thing. Figure 10 is a photomicrograph of an albite porphyroblast from the Peters Creek schist. Figure 11 is a projection of this porphyroblast and its included muscovite flakes. The only maximum is in (010). Figure 12 is a dia-

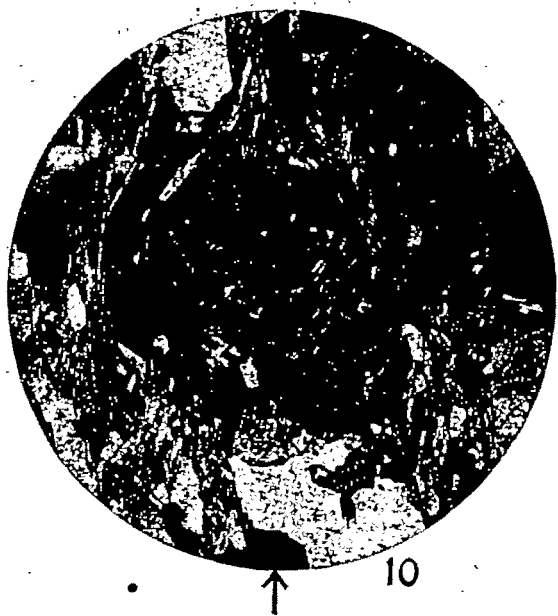


Fig. 10. Photomicrograph of an albite porphyroblast from the Peters Creek schist. Note the high angle that the mica of the trend makes with the mica of the groundmass. Specimen P. C.-2. Crossed nicols. $\times 85$.

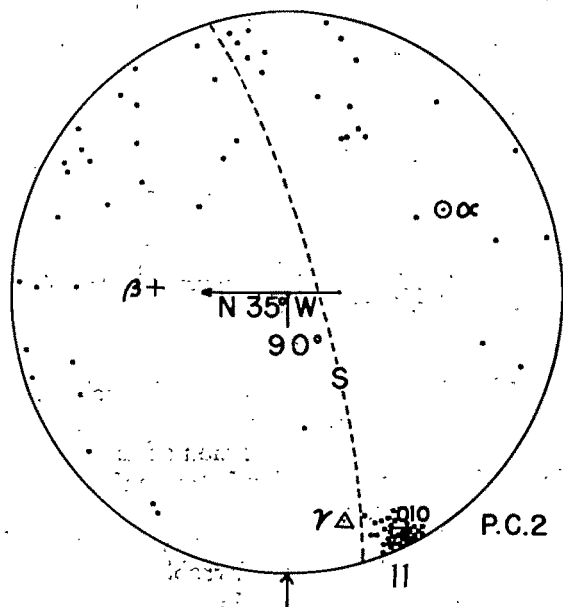


Fig. 11. Projection of the albite crystal shown in Fig. 10 and the poles of its included muscovite flakes.

gram prepared from the mica of the groundmass of this same specimen. It shows that the mica of the trend stands almost normal to that of the groundmass, which can also be seen in the photomicrograph, Fig. 10.

An oligoclase porphyroblast from a specimen of the granite streamer southeast of Darlington, Fig. 13, shows strong maxima in (010) and (001). The mica outside of the porphyroblasts of this specimen is mostly biotite and the crystals

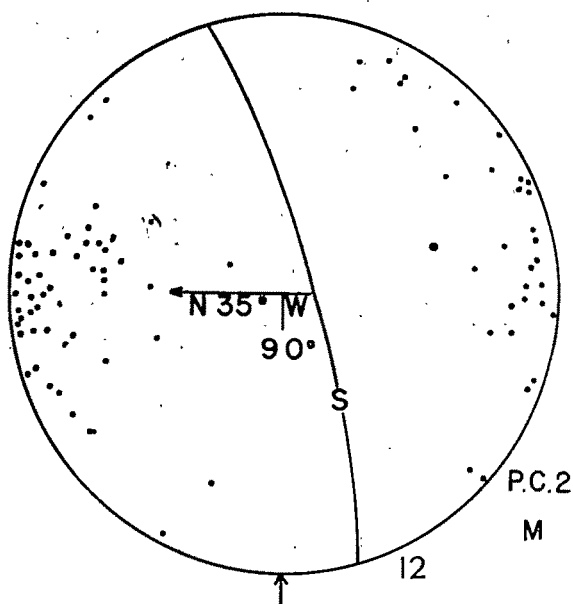


Fig. 12. Poles of 87 mica flakes in the groundmass around the porphyroblast represented in Figs. 10 and 11.

are much larger than are the muscovite inclusions. They are also somewhat crumpled, whereas the inclusions are clear and sharp. Figure 14 shows the orientation of these biotites, which have their maximum concentration between the two maxima of the muscovite inclusions.

This difference in size and character between the mica inside and outside of the plagioclase porphyroblasts is rather common in these rocks and suggests that the inclusions were probably formed later than the host rather than earlier.

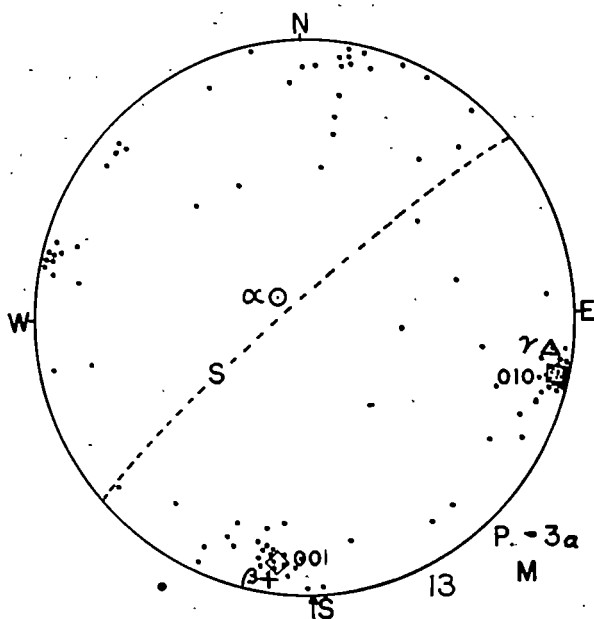


Fig. 13. Projection of an oligoclase porphyroblast from a streamer of granite in gneiss southeast of Darlington. Specimen P.-3a.

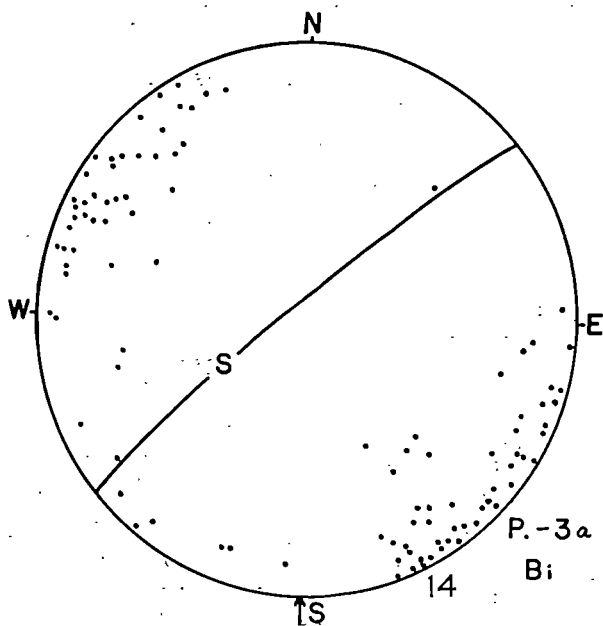


Fig. 14. Poles of 101 biotite flakes from the groundmass of specimen P.-3a.

This control of trends by the lattice of the host should not be applied too generally. There are doubtless some examples of true relict structures. The trends described by Singewald⁹ may be true relict structures, although there is another possible explanation. Cloos¹⁰ observes that the folded trends occur where there is much mica in the groundmass, i.e. in zones that are well lubricated and in which there may have been intense differential movement. If the mica had formed along feldspar cleavages, it conceivably could have been crumpled by later movements.

SIMILAR EUROPEAN OCCURRENCES.

Drescher¹¹ has described what he believes to be true relict structures, although in two of the three diagrams that he gives, the maximum concentration of the microlites is very near to a major cleavage of the feldspar.

Andreatta has done more detailed and extensive work on this problem than anyone else. In intrusive rocks¹² he finds that practically all the mica is controlled by the lattice of the feldspar. The (001) and (010) planes commonly contain most of the mica, but (110) is sometimes effective.

In orthogneiss¹³ he finds that the orientation is less perfect with respect to the lattice of the feldspar, some of the mica flakes apparently being related to the fabric of the rock rather than the host feldspar grains.

From a paragneiss¹⁴ Andreatta describes feldspar porphyroblasts that contain relicts of two older structures that possibly are related to two different periods of metamorphism.

⁹ Op. cit.

¹⁰ Cloos, E.: Personal communication.

¹¹ Drescher, F. K.: Über Mikroklinholoblasten mit Grundgewebseinschlüssen, Internregelung von Biotit und einige diesbezügliche genetische Erwägungen, Notizbl. des Vereins für Erdkunde u. der Hess. Geol. Landesanstalt zu Darmstadt, 5 Folge, 10 Heft, pp. 246-269, 1927. Also, Zur Genese der Diorite von Fürstenstein, Neues Jahrb. Mineral. Geol., Beilage Band, A, 60, 477-494, 1930.

¹² Andreatta, C.: Disposizione dei microliti micacei in plagioclasti di rocce intrusive (Analisi strutturali di rocce, IV), Periodico mineral. (Rome), 5, 1-21, Plates 1 and 2, 1934.

¹³ Andreatta, C.: Analisi strutturali di rocce metamorfiche, III. La disposizione dei microliti micacei nei plagioclasti di ortogneis, Periodico mineral. (Rome), 4, 1-20, Plates 1-6, 1933.

¹⁴ Andreatta, C.: La formazione gneissico-kinzigitica e le oliviniti di Val d'Ultimo, Mem. del Museo di Storia Naturale della Venezia Tridentina, 3, fasc. 2, 31-42, 1935.

CONCLUSIONS.

For the albite trends of the Port Deposit granodiorite complex and surrounding formations, the following conclusions appear to be valid:

1. The mica inclusions are directly related to the lattice of the host feldspar porphyroblasts.
2. They are indirectly related to the present fabric of the rock in that the cleavages controlling the trends have been developed in the zone of the *s*-planes of the rock.
3. These trends are not relict structures and therefore do not indicate more than one period of metamorphism.
4. Since there are similar trends in the plagioclase porphyroblasts in all the rocks of Ordovician age or older, in this region, their presence cannot be used as a criterion of age relations.
5. The inclusions of the trends were probably formed during late hydrothermal activity by solutions permeating the plagioclase along planes of greatest accessibility.

THE SYSTEM, WATER — BORON OXIDE.¹

F. C. KRACEK, G. W. MOREY, AND H. E. MERWIN.

ABSTRACT.

Measurements of the solubilities were made to establish the equilibrium relations over the whole range of compositions in the system composed of water and boron oxide.

The crystalline phases occurring in the system are found to be ice, H_3BO_3 , three modifications of HBO_2 in monotropic relation to one another, and crystalline B_2O_3 . Solubility curves have been determined for each of these phases, and the properties of the new phases are described. The $P-T-X$ relations for saturated solutions were evaluated. These are of importance for geochemistry.

Boron oxide is a constituent of many minerals which occur in nature under conditions indicating widely differing modes of origin. Nearly all these minerals are attacked by aqueous solutions. The more soluble compounds occur in economically important quantities in salt beds and in desert lake and salt marsh deposits. Fumarolic and hot spring effluvia in many cases disengage large quantities of boric acid, not only in solution, but also in the vapor. Thus, in the suffioni of Tuscany, the steam issuing from the ground carries up to 0.5 g. of H_3BO_3 per liter at pressures reaching about 5 atm., the temperature being near $190^\circ C$. The boric acid is deposited here in the free state as the mineral sassolite, H_3BO_3 . Because of the frequent occurrences of boron compounds in nature, the study of the heterogeneous equilibria in the system, $H_2O-B_2O_3$, is of direct interest for geophysical chemistry.

In industry, the most important use of boron oxide and its compounds, from the standpoint of heterogeneous equilibria, is in the ceramic and the glass industries, mainly as a constituent of certain special purpose glasses. Here the presence of B_2O_3 imparts toughness and other beneficial properties, such as low coefficient of expansion, and resistance to devitrification. The special character of the glasses derives from the unique prop-

¹ Paper presented at the spring meeting of the American Chemical Society at Dallas, Texas, April 19, 1938.

erties of vitreous B_2O_3 and from its influence upon the properties of vitreous silica in the glass melts. Crystalline B_2O_3 is of interest here primarily for the reasons that its melting point is low, and that its crystallization is essentially a specialized process.

The published information on the equilibrium relations in this system is highly fragmentary. Aside from the ordinary boric acid, H_3BO_3 , various other compounds have been reported, mostly on grounds that will not bear critical examination. Of these, the metaboric acid, HBO_2 , is the only one for which a definite proof has been given. However, as we shall see, metaboric acid itself crystallizes in three modifications which stand in monotropic relation to each other; only two of these modifications appear to have been obtained before, and what is more important, without the realization that they were different crystalline phases. Further confusion arises from the failure of some workers to differentiate adequately between the amorphous and the crystalline states of matter. Until very recently, B_2O_3 has been known only in the vitreous condition, and hence, the various older statements concerning its "melting point" are obviously without meaning. The reason for many of these uncertainties lies in the fact that in many cases adequate criteria have not been employed to identify the crystalline products when obtained.

In working with the solutions in this system, there are encountered experimental difficulties which are more or less unique, and characteristic of the phases involved: At the higher B_2O_3 concentrations the solutions are highly viscous; the attainment of equilibrium is slow, not only for this reason, but also, and in greater measure, because of the inertness of behavior of some of the crystalline compounds in solution.

The work outlined in connection with this system at this Laboratory comprises the determination of the necessary data for the evaluation of the P—T—X relations, as far as may be practicable. The data presented in this paper include an experimental study of the solubilities for the entire range of compositions, and a correlation of these measurements with existing information on the vapor pressures, resulting in the evaluation of the vapor pressure relations for the saturated solutions. The optical and other properties of the various crystalline phases encountered are also given. Further work is in progress.

SOLUBILITY DETERMINATIONS.

The choice of method for the measurement of solubilities in this system is limited, for several reasons. Firstly, the vapor must be confined, since for most of the system, the vapor pressures at the liquidus are in excess of one atmosphere. Secondly, it is not practicable to separate the solution from the crystal phases by filtration, because the viscosities are generally too high. Thirdly, equilibrium is attained slowly for some of the phases, and hence, it is an advantage to follow the progress of the experiment visually. Finally, simplicity of method is desirable, when it can be secured without sacrificing accuracy.

For these reasons, we have employed the well known method of sealed tubes, in which solutions of known gross composition are heated at various temperatures, and a measurement is made of the temperature at which the last crystal dissolves in the saturated solution. The composition may be evaluated accurately from the weight of the constituents used, or by subsequent analysis.

The method has already been tested adequately in this Laboratory at elevated temperatures.² The apparatus for heating the sealed tubes consists of a copper-lined air bath thermostat whose temperature can be controlled with a precision of $\pm 0.02^\circ \text{C}$. at any temperature up to about 600°C . The thermostat is provided with windows for observation, and with means for circulating the air and rotating the solubility tubes to obtain efficient stirring of the contents. The temperatures are measured by calibrated thermocouples whose emfs. are read with the aid of a Wulf-Feussner potentiometer.

Pyrex chemical resistant glass tubes of 8 to 10 mm. internal diameter are used as containers for the solutions. The strength of such tubes is adequate to withstand the relatively low pressures developed by the vapor at the liquidus in this system, and the large diameter has the advantage of facilitating the stirring of the viscous solutions. The stirring may be further aided by adding gold beads to the contents of the tubes.

The principal objection to this method is the possibility of corrosion of the glass tubes. This was found to be negligible throughout the system, although slight etching was observed

² Kracek, F. C.: *J. Phys. Chem.*, 35, 417, 947, 1931; *J. Am. Chem. Soc.*, 53, 2609, 1931; *J. Wash. Acad. Sci.*, 26, 307, 1936.

with the highest B_2O_3 composition. On analysis it was found, however, that the impurities thus introduced amounted to less than 0.1 per cent.

TABLE I.

The system, $H_2O-B_2O_3$.

No.	% B_2O_3		Liquidus temp. °C.					$(p/p_0)_1$
	Weight	Mole	H_2BO_3	HBO_2 III	HBO_2 II	HBO_2 I	B_2O_3	
1	8.20	2.26	65.2	0.954
2	10.87	3.06	79.5935
3	15.51	4.53	99.7901
4	17.72	5.28	107.8883
5	20.66	6.31	117.1858
6	23.84	7.49	126.7830
7	27.48	8.93	136.3795
8	30.85	10.35	143.3761
9	35.03	12.24	151.5717
10	39.79	14.60	159.4663
11	44.01	16.90	163.4612
12	48.63	19.67	167.3553
13	49.15	22.10	169.8504
14	55.75	24.58	170.1456
15	56.30	25.00	171.1	190448
16	56.30	25.00	170.9448
17	56.30	25.00	171.0	190448
18	58.81	26.97	170.8	201413
19	61.14	28.93	169.6	212379
20	62.34	29.98	169.0	172.0	213361
21	65.84	33.27	166.1	181.3	219309
22	69.65	37.25	159.6	189.4	225252
23	71.31	39.13	192.5	227228
24	72.30	40.30	164.0	194.5212
25	75.05	43.76	198.0	232166
26	76.01	45.04	199.2	233153
27	76.98	46.38	173.5	200.0	234137
28	77.93	47.74	200.6123
29	79.45	50.00	176.1	200.9101
30	79.45	50.00	175.9	200.9	236101
31	79.45	50.00	175.9	200.9101
32	79.35	49.85	200.9102
33	79.40	49.92	200.9	235.6102
34	81.97	54.05	173.7	199.7	235	233	.069
35	83.75	57.14	170.0	197.5	231	253	.053
36	85.23	59.89	194.8	230	273	.040
37	86.66	62.69	159.5031
38	87.13	63.66	298	.028
39	87.65	64.74	303	.025
40	89.86	69.63	334	.016
41	92.36	75.78	363	.009
42	92.96	77.35	367	.007
43	95.31	84.01	392	.004
..	100.0	100.0	450	...

Reagents.

The compositions studied were made up quantitatively by enclosing in the sealed tubes known weights of the constituents. Although it would have been feasible to use the end components H_2O and B_2O_3 throughout the system as reagents, it was found preferable to use mixtures of H_3BO_3 with water, or with anhydrous B_2O_3 glass, depending upon the desired composition. In some cases HBO_2 was also used as reagent.

The H_3BO_3 was reagent grade boric acid further purified by recrystallization.

Anhydrous B_2O_3 glass was prepared by heating "boric acid anhydride," reagent grade, to 1300°C . Evaporation with HF , and with methyl alcohol and HCl mixture left a negligible residue in each case, indicating less than 0.05 per cent impurities.

Metaboric acid in a coarsely crystalline condition (HBO_2II , vide infra) was prepared by heating recrystallized H_3BO_3 at $130\text{--}140^\circ\text{C}$. for 2 or 3 days in vessels from which the escape of vapor was partially impeded. Analysis showed this to be generally 79.40 ± 0.05 per cent B_2O_3 ($\text{HBO}_2 = 79.45$).

The Solubility Relations.

The crystalline phases occurring at the liquidus in the system are ice, orthoboric acid (H_3BO_3), three modifications of metaboric acid (HBO_2I , II , III), and crystalline B_2O_3 . The solubility curve for ice extends only from the freezing point of ice to the cryohydric point at -0.76°C ., and needs no further consideration. Measurements have been made for all the other phases. The data are given in Tables I and II, and are graphically illustrated in Fig. 1.

TABLE II.

Invariant points, $\text{H}_2\text{O-B}_2\text{O}_3$.			
Phase reaction	Mole % B_2O_3	Temp. $^\circ\text{C}$.	(p/p_0) ₁
Melting of ice	0.0	0.0	1.0
Eutectic ice + H_3BO_3	0.333	-0.76	0.994
Melting of H_3BO_3	25.00	170.9 ± 0.2	.448
Incongruent melting $\text{H}_3\text{BO}_3 \rightleftharpoons \text{HBO}_2\text{I} + \text{liq.}$	21 ± 1	169 ± 1	.523
Eutectic $\text{H}_3\text{BO}_3 + \text{HBO}_2\text{II}$	29.3 ± 0.2	169.6 ± 0.2	.373
Eutectic $\text{H}_3\text{BO}_3 + \text{HBO}_2\text{III}$	38.0 ± 0.2	158.5 ± 0.5	.242
Melting of HBO_2I	50.00	236 ± 1	.101
Melting of HBO_2II	50.00	200.9 ± 0.5	.101
Melting of HBO_2III	50.00	176.0 ± 0.2	.101
Eutectic $\text{HBO}_2\text{III} + \text{B}_2\text{O}_3$	50.0 ± 0.5	176.0 ± 0.2	.101
Eutectic $\text{HBO}_2\text{II} + \text{B}_2\text{O}_3$	51.8 ± 0.5	200.5 ± 0.5	.086
Eutectic $\text{HBO}_2\text{I} + \text{B}_2\text{O}_3$	55.1 ± 0.5	235 ± 2	.063
Melting of B_2O_3	100.00	450 ± 2	.000

1. *The Solubility of Orthoboric Acid.* The properties of this compound which occurs in nature as the mineral sassolite are known in considerable detail, and its crystal structure has been determined.⁸ It crystallizes in plates and prisms, and it

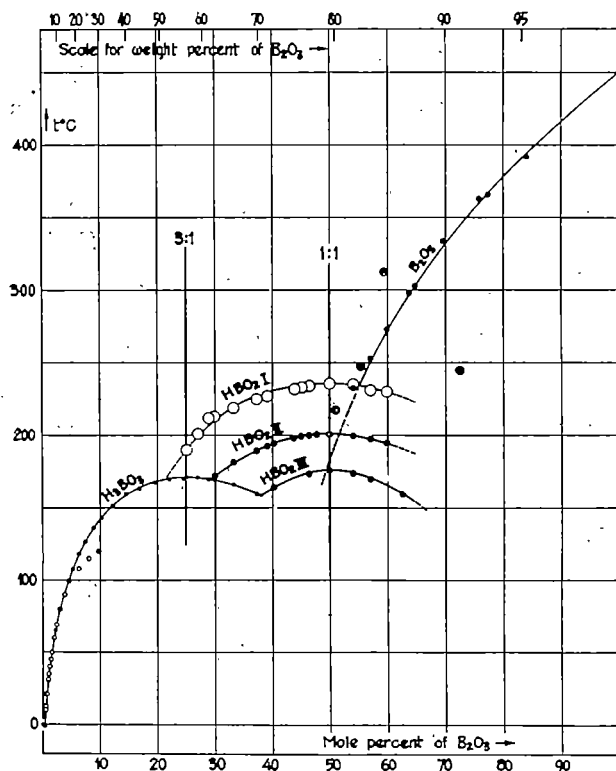


Fig. 1. Solubility diagram for the system, $\text{H}_2\text{O} - \text{B}_2\text{O}_3$. Open circles on and near curve for H_2BO_3 , Nasini and Ageno; crossed circles near curve for B_2O_3 , McCulloch; all other points by the authors. McCulloch's m. p. for B_2O_3 , not indicated in figure, is $460-470^\circ$. The curve drawn for the solubility of B_2O_3 represents equation (1).

dissolves readily with little tendency to form highly supersaturated or undersaturated solutions. The solubility has been studied from the cryohydric point to 120°C . by Nasini and Ageno,⁴ Sborgi and Ferri⁵ and others. Owing to the methods

⁸ Zachariasen, W. H.: *Z. Krist.*, 88, 150, 1934.

⁴ Nasini and Ageno: *Gazz. chim. ital.* 41-I, 131, 1911.

⁵ Sborgi and Ferri: *Mem. accad. Lincei* (5) 13, 586, 1922.

employed, the published data are not accurate above 100°C . Our results for the solubility of this compound yield a curve having a flat maximum at the melting point, $170.9^{\circ} \pm 0.2^{\circ}\text{C}$.⁶ A part of this curve is metastable with respect to two of the forms of metaboric acid, discussed in the next section.

2. *The Solubilities and Crystallization of the Metaboric Acids HBO_2I , HBO_2II , HBO_2III .* Metaboric acid is capable of crystallizing in three distinct modifications with very different properties. This has been overlooked by previous workers, although the fact that the three phase pressures for the dissociation of H_3BO_3 to HBO_2 and water vapor, as measured by different authors, fall upon two separate $P-T$ curves proves that two of these modifications at least should have been recognized. This will be discussed in detail at a later point.

As may be seen from the solubility diagram, the three modifications exist in monotropic relation to each other, their melting points being as follows: HBO_2I $236^{\circ} \pm 1^{\circ}\text{C}$., HBO_2II $200.9^{\circ} \pm 0.5^{\circ}\text{C}$., and HBO_2III $176.0^{\circ} \pm 0.2^{\circ}\text{C}$.

HBO_2III crystallizes almost as readily as H_3BO_3 . The other two forms grow much more slowly, HBO_2I in particular being very inert in behavior.

When H_3BO_3 is dehydrated in open vessels at about 130°C ., the dehydration product at first consists of flaky crystals of HBO_2III admixed with unconverted H_3BO_3 ; on continued heating the H_3BO_3 gradually disappears and the HBO_2III recrystallizes to coarsely crystalline HBO_2II . At this stage the dehydration stops promptly at the composition HBO_2 unless the time is excessive, or the temperature is raised above 150°C . Under these conditions the dehydration slowly continues, yielding a highly viscous liquid whose composition lies between HBO_2 and B_2O_3 . As we shall see shortly, this liquid occasionally carries a more or less abundant quantity of the stable modification of metaboric acid, HBO_2I , and in some such cases may give rise to spontaneous crystallization of B_2O_3 .

When the coarsely crystalline HBO_2II is melted in the sealed tubes, there usually remain in the liquid a few brilliant crystal-lites of HBO_2I . These grow with extreme reluctance, the complete crystallization of the contents of a tube requiring sometimes many weeks for completion. We have found no way to accelerate the growth; conversely, the dissolution of

⁶ Von Stackelberg, Quatram and Dressel, Z. Elektrochem., 43, 14, 1937, give 170°C . for the m. p. of H_2BO_2 and 203°C . for HBO_2 .

this phase is also a slow process, the crystals being very slowly attacked by water at ordinary temperature. In consequence of this, it is possible to isolate the phase in pure form by leaching out the more rapidly soluble constituents of a mixture in which it occurs and collecting the crystals upon a filter. This was done for measurement of the density.

When sealed tubes containing melted HBO_2 are quickly cooled, the contents at first solidify to a glass, which then gradually becomes milky owing to the incipient crystallization of HBO_2III . On raising the temperature, the contents quickly crystallize to an opaque white mass which melts sharply at 176.0°C. ; the melting point of HBO_2III .

The recrystallization of HBO_2III to the more stable forms, HBO_2II or HBO_2I in sealed tubes, depends on the presence of nuclei of the more stable phases. Prolonged heating above 201°C. causes the melt to become sterile with respect to HBO_2II , and HBO_2III can then be kept unaltered in such tubes for indefinite periods. Prolonged heating at 170° - 175°C. usually, however, results in recrystallization to HBO_2II , and in many cases also produces an abundant quantity of HBO_2I . It should be mentioned at this point that the HBO_2I , if completely absent originally, can be induced to crystallize in this way. On the other hand, heating HBO_2II in sealed tubes at just below its melting point does not tend to initiate the spontaneous growth of HBO_2I .

The compositions of the different modifications of metaboric acid were established by analysis, titrating weighed samples with a standard $\text{Ba}(\text{OH})_2$ solution in the presence of mannitol, using phenolphthalein as indicator.

In the case of HBO_2III the method was an indirect one, being combined with the deductions from the solubility relations. Both the synthetic and the analyzed compositions representing HBO_2 gave the maximum liquidus temperature for HBO_2III , and particularly, determinations on solubility tubes filled with analyzed HBO_2II prepared by dehydration in open vessels yielded, after melting the HBO_2II , quenching, and recrystallization to HBO_2III , a homogeneous product which melted at $176.0 \pm 0.2^\circ \text{C.}$

HBO_2II prepared by dehydration of H_3BO_3 in open vessels at 130° - 140°C. was consistently found to be of nearly the theoretical composition, analyses giving 79.40 ± 0.05 weight per cent B_2O_3 , as against the theoretical 79.45.

HBO₂I was prepared for analysis in sealed tubes. In this case, since there was a possibility that the crystals might be some other hydrate, such as H₂B₄O₇, the composition from which the phase was crystallized for analysis was chosen purposely to be different from HBO₂, being 80.2 weight per cent B₂O₃. After several weeks crystallization, the tubes contained a quantity of the desired crystals and some uncrystallized solution. The solution was drained off into one end, and the tubes were then cut open and the contents analyzed. The contents of the upper portion of the tubes were found to be 79.6 ± 0.1 per cent B₂O₃, i.e., practically pure HBO₂. The uncrystallized solution together with the crystals deposited in the lower portion always had a higher B₂O₃ content than the original 80.2 per cent B₂O₃ mixture, typical results being 80.8 and 81.2 per cent B₂O₃. The results of these analyses prove therefore that the crystalline phase in question has the composition of HBO₂.

The solubilities of the three modifications of metaboric acid are represented, as may be seen from Fig. 1, by three nearly parallel curves with flat maxima at the composition of the acid. The determination of the separate solubility curves, though tedious from the standpoint of the time involved, presents no particular difficulties. The most important precautions to observe are to make the stirring as efficient as possible, to give ample time for equilibrium to be attained, and especially in the case of HBO₂III, to keep the other two modifications from growing while the determination is being made. The time necessary for saturation with HBO₂III is short, 30 minutes to one hour being ample at each constant temperature even for the viscous solutions on the B₂O₃ side of the compound. With HBO₂II, saturation is obtained more slowly, but here also, the time required is not excessive. With HBO₂I, however, at least 48 hours must be allowed at each temperature, and even then, equilibrium is sometimes not certain in the more viscous solutions. Efficient stirring is of the utmost importance. The behavior of this phase in aqueous solutions is somewhat comparable in speed to that of crystalline quartz in alkali silicate melts, and may be more sluggish.

In solutions richer in B₂O₃ than HBO₂, the solubilities were determined over a moderate range of compositions in the region metastable with respect to crystalline B₂O₃. Determinations in this region are of interest for the reason that B₂O₃ tends to crystallize spontaneously from these solutions in the presence of crystals of HBO₂I.

3. *Crystalline Boron Oxide.* The phase which was later identified as crystalline B_2O_3 was first obtained in our solubility tube 38 (63.66 mole per cent or 87.13 weight per cent B_2O_3), made up from H_3BO_3 and anhydrous B_2O_3 glass. After dissolving the glass in the solution, the tube was set aside for several months at about $175^\circ C.$ to crystallize. When crystals had developed, it was found that, in addition to the metaboric acids, there was present a new phase whose liquidus at this composition is $298^\circ \pm 1^\circ C.$ At that time the solubility relations for the other phases were known only in outline; however, it was found that, in other experiments on the liquidus of what we now know to be HBO_2 I in B_2O_3 rich solutions, the same phase usually began to precipitate before all the HBO_2 I dissolved, and several points on its liquidus were determined at that time.

Later, this phase was isolated by settling and draining off the liquid. The material isolated was then used in seeding experiments, which furnished some very important information.

The seed was first added to anhydrous B_2O_3 glass, which was heated for several months at various temperatures. The results were completely negative, the added crystals merely remaining suspended in the softened glass in a wholly inert condition. This was also the case when the seed was added to glass containing about one per cent of water in a sealed tube; the seed melted when the temperature was raised to $430^\circ \pm 10^\circ C.$

On adding the seed to a mixture containing about five per cent of water in a sealed tube, a moderately rapid growth of crystals was observed, seemingly complete crystallization being obtained in 24 hours at $250^\circ C.$

When the seed was added to other compositions richer in water, relatively rapid crystallization took place, and the various points on the liquidus were then determined.

The seed was also added to HBO_2 II in open crucibles. As soon as the metaboric acid began to melt, a gentle bubbling started, accompanied by a clouding of the melt, and in less than 24 hours the mass was changed to a rock-like aggregate of minute crystals cemented by a small quantity of glass.

The crystals used for seeding were comparatively well developed, and their optical properties were determined (*vide infra*). The crystals obtained in the open crucibles, and in the short-time experiments in sealed tubes, are extremely minute, and are unsuitable for examination. By X-ray diffraction, all these

crystals were shown to be alike, and different from the other phases, and the preparations obtained in the open crucible experiments were analyzed. After 18 hours heating near 205° C. the B_2O_3 content was found to be near 99 weight per cent; after heating for more than 40 days at 400° C. the analysis gave 100.0 ± 0.1 per cent B_2O_3 , with very little glass visible under the microscope.

Towards the end of our experimental work McCulloch⁷ was the first to announce the spontaneous crystallization of boron oxide from partially dehydrated boric acid in open vessels. His results on large batches presented a new aspect of the problem for the reason that experiments on small batches analogous to his had always given us only a more or less dehydrated vitreous phase. On duplicating his procedure more or less closely, it was found at first that no crystallization of B_2O_3 was obtained except in one experiment out of a number. In this particular experiment it was noted that, as the dehydration proceeded beyond the HBO_2 stage, there remained a small incrustation of HBO_2 I crystals on the walls of the container. When this deposit was mixed with the melt and heating was continued at 210° C., the melt clouded in a short time, and in 24 hours was found to be almost completely crystallized.

To confirm this observation we performed parallel experiments with two samples of HBO_2 II which originally contained no HBO_2 I, as determined by melting a separate sample in a sealed tube. To one of the samples was added a small quantity of HBO_2 I; the other sample was used as control. The two samples were heated at 205° C. separately, to avoid any possibility of contamination. In the material with HBO_2 I added, there was observed a clouding of the melt shortly after the HBO_2 II melted, and in less than 3 days the sample was crystallized almost completely to B_2O_3 . The control sample merely continued to dehydrate, with no crystallization in more than a week.

A final conclusive experiment was performed starting with recrystallized H_3BO_3 . From the solubility relations we know that as the gross B_2O_3 content of the system exceeds that of H_3BO_3 , the stable phases in coexistence at temperatures below the incongruent melting point of H_3BO_3 to HBO_2 I and liquid are HBO_2 I and H_3BO_3 , up to the composition HBO_2 . The other modifications of HBO_2 may also be present simul-

⁷ McCulloch, L.: J. Am. Chem. Soc., 59, 2650, 1937.

taneously, but that is non-essential. If the dehydration of H_3BO_3 is performed slowly, HBO_2I should be present, at least in small amounts. That is what is actually observed. The H_3BO_3 in this experiment was slowly dehydrated in a closely covered flask for a week at 120°C ., after which the temperature was raised at 10° intervals daily to 200°C . At the end of this time the flask contained a viscous melt from which had settled out a relatively large quantity of HBO_2I crystals. The melt also showed a faint clouding, but crystallization was not proceeding at an appreciable rate, which is in accord with our experience, that B_2O_3 does not crystallize readily from highly dehydrated viscous melts. To reduce the viscosity, a roughly calculated quantity of the purified H_3BO_3 was added to bring the composition to near HBO_2 , and heating was continued with the oven set at 200°C . In a short time the added H_3BO_3 was converted to HBO_2 . When this melted, the previously observed clouding was found to increase at a rapid rate accompanied by quiet ebullition. The crystallization of B_2O_3 then completed itself in about 36 hours.

In all other experiments in which HBO_2I was totally absent, the dehydration resulted in a viscous melt with no crystallization, and in particular, we have never found HBO_2II or HBO_2III to initiate the spontaneous crystallization of B_2O_3 , whether in open vessels, or in sealed tubes.

To recapitulate the results of our various experiments on the crystallization of B_2O_3 , it may be stated that:

(1) the crystallization is not spontaneous in clear solutions;
 (2) the crystallization has been initiated by crystals of HBO_2I (compare under properties of crystalline B_2O_3 below) but not by HBO_2II or HBO_2III ;

(3) in sealed tubes it is initiated below the eutectic temperature for HBO_2I and B_2O_3 , and growth seems to occur most rapidly when the liquidus temperature for HBO_2I is just slightly exceeded in the case of solutions somewhat richer in B_2O_3 than the eutectic, so that the crystals of HBO_2I are melting in the liquid;

(4) in open vessels the initiation occurs at these or lower temperatures, owing to the continuous dehydration of the melt and the consequent tendency toward dissociation of HBO_2I . The quadruple point (HBO_2I — B_2O_3 —solution—vapor) pressure at the eutectic (235°C .) is calculated to be 1.9 atm., and the corresponding three phase pressure for the dissociation of

HBO₂I reaches 1 atm. in the neighborhood of 200° C. (see Figs. 3 and 4 and Table II);

(5) when the crystallization is initiated by seeding or by the presence of HBO₂I, the speed is relatively high in solutions or melts whose composition is near HBO₂, but becomes very small when the composition is near B₂O₃. The viscosity of the solutions changes enormously over this range of composition, and may account for some of the observed reluctance towards crystallization from high B₂O₃ concentrations. It is problematical whether it accounts for all of it, and in this connection, Zachariasen's picture of the constitution of B₂O₃ glass⁸ is suggestive. It is reasonable to assume that the extended networks of atoms characteristic of the vitreous oxide are more limited in extent and more easily subject to rearrangement in the more highly hydrated melts or solutions near HBO₂ than in the anhydrous condition.

From the above discussion it is easy to see that the spontaneous crystallization of B₂O₃ is not a simple process, depending as it does on the previous formation of HBO₂I. The saving feature in the process is that HBO₂I is capable of existence over a very great extent of the system, and that its nucleation presents no particular difficulties.

The melting point of E₂O₃ was determined by the method of quenching, as used in this Laboratory for the study of phase equilibria in silicate systems. The value obtained is 450° ± 2° C., 3 days being allowed at each temperature for the attainment of equilibrium. The absence of crystals was determined microscopically. The value obtained is lower than McCulloch's 460°—470° C., but is in essential agreement with it, as contrasted with the previously reported value of 294° C. by Cole and Taylor.⁹ The material employed in our determination had been crystallized in a platinum crucible for more than 40 days at 400° C. and was found by analysis to be 100.0 ± 0.1 per cent B₂O₃. The crystallized material carried only a small quantity of glass.

The solubility determinations in sealed tubes were not extended beyond 95.31 weight (84.01 mole) per cent B₂O₃, for two reasons. One was that beyond this point it becomes increasingly more difficult to stir the solutions because of the extremely high viscosity at the liquidus, so that there can be no

⁸ Zachariasen, W. H.: J. Am. Chem. Soc., 54, 3841, 1932.

⁹ Cole and Taylor: J. Am. Ceram. Soc., 18, 55, 1935.

assurance of equilibrium having been reached; the second reason was that a slight corrosion of the tubes is observed at this and higher concentrations of B_2O_3 , and it was felt that points determined in the remaining region would be of uncertain accuracy.

The solubility values for B_2O_3 fall on a curve represented by the empirical equation

$$(1) \quad \log N_2 = \frac{119.1}{4.574 T} - 1.700 \log T + 0.002485 T + 3.0278$$

where N_2 is the mole fraction of B_2O_3 for H_2O and B_2O_3 as components, and T is the Kelvin temperature. On applying deductions from Gibbs' method of dealing with heterogeneous equilibria, the slope of this curve yields

$$(2) \quad \Delta H = 2.303 T \left(\frac{d \log N_2}{dT} \right) \left(N_2 \frac{d \mu_2}{d N_2} \right)_{p, T}$$

$$(2') \quad \Delta H = 2.303 RT^2 \left(\frac{d \log N_2}{dT} \right) \left(\frac{d \log a_2}{d \log N_2} \right)_{p, T}$$

which, on introducing numerical values, becomes

$$(2'') \quad \frac{\Delta H}{\left(\frac{d \log a_2}{d \log N_2} \right)_{p, T}} = -119.1 - 3.376T + 0.011364T^2 \\ = 3380 \text{ cal./mole at } 723^\circ \text{K (} 450^\circ \text{C.)}$$

In the above equations μ_2 and a_2 are the chemical potential¹⁰ ("partial molal free energy" of Lewis) and the activity of B_2O_3 (standard state $N_2 = 1$) in solution, and ΔH is the differential heat of solution of crystalline B_2O_3 . Since we have no experimental data as yet for ΔH or μ_2 as functions of the concentration, it is at present impossible to evaluate the two quantities separately.

If the solubilities are expressed in terms of N_2' , N_2' being the mole fraction of B_2O_3 with HBO_2 and B_2O_3 as components, the plot of $\log N_2'$ against $1/T$ is a straight line over a

¹⁰ We employ μ_i in the sense defined by Gibbs, as the chemical potential per unit mass of component i , which in this case is the mole. μ_i is then identical with Lewis' \bar{F}_i or Guggenheim's \bar{G}_i when P , T , and N are the variables.

wide range of compositions (from $N_2' = 0.3$ to 1.0). From the slope of this line we obtain

$$(2''') \quad \frac{\Delta H}{\left(\frac{d \log a_2'}{d \log N_2'} \right)} = 2.303 RT^2 \left(\frac{d \log N_2'}{dT} \right) \\ = 6720 \text{ cal./mole,}$$

or, in round numbers, 97 cal./g., a value almost exactly double that obtained from equation (2'') at the melting point. This is the heat of fusion of B_2O_3 calculated on the assumption that $a_2' = N_2'$, that is, that Raoult's law holds in terms of N_2' over the region for which the curve is a straight line. The assumption appears to be a reasonable one, and on its basis it follows that $a_2 = k_2 N_2^2$, $a_1 = k_1 N_1^2$ at the neighborhood of $N_2 = 1$, k_1 and k_2 being constants determined by the choice of standard state. This is of use in connection with the vapor pressure data, as we shall see shortly.

The calculated heat of fusion of B_2O_3 , 97 cal./g., is large, the corresponding entropy of fusion being 9.3 entropy units per mole, a value about twice that for the melting of ice. We hope to have an experimentally measured value in the near future.

THE VAPOR PRESSURE RELATIONS.

It is well known that the boric acids are somewhat volatile.¹¹ The distribution of the components between the solution and vapor is such, however, that the partial pressure of B_2O_3 (or, of the acids) in the vapor is small in comparison with that of water, and hence, for purposes of calculation, the error introduced by assuming the total pressure to be equal to the partial pressure of water is relatively small.

The activity of water, a_1 , in the saturated solutions of a given binary system may be expressed by

$$(3) \quad \frac{d \ln a_1}{dT} = \left(\frac{d \ln a_1}{dT} \right)_x + \left(\frac{d \ln a_1}{dX_1} \right)_T \left(\frac{dX_1}{dT} \right)_p$$

On comparing this with the expression derivable on the basis

¹¹ Von Stackelberg, Quatram and Dressel (op. cit.) contribute an extensive discussion on this question.

of Gibbs' theory of heterogeneous equilibria (second component non-volatile),

$$(3') \quad RT^2 \frac{d \ln a_1}{dT} = (H''_0 - H'')_1 + \frac{X'''_1 - X''_1}{X'_1 - X''_1} (H' - H'')$$

(accents relate to phases, subscripts to components), it is seen that the first term of (3) contains the heat of dilution of the solution by the addition of the liquid solvent, and that the second term contains the much larger heat of solution of the crystalline solute.^{12, 18}

The heat of dilution is usually small, and its contribution in influencing the vapor pressure of a solution of a given concentration is small enough to have given rise to the generalization known as von Babo's law. In exact measurements its effect is perceptible, and normally must be taken into consideration.

Confining the attention to the second term of equation (3), and comparing with (3'), we see that if the solubility is known as a function of the temperature, and if the activity or the vapor pressure is known as a function of the concentration at various temperatures, then the correlation of the pressure—temperature—concentration relations of saturated solutions may be evaluated. For an accurate correlation the heats of dilution are needed, as was pointed out in the preceding paragraph; if they are not known, the calculation will still be correct in principle, but will be numerically somewhat inaccurate.

In the case of the system $H_2O-B_2O_3$, no heats of dilution are available, and the data upon which to base the vapor pressure-composition relations are also very incomplete. Enough is known, however, to make a simplified calculation which turns out to be accurate to probably somewhat better than ± 2 per cent in the activity values for the major part of the system. Throughout this calculation we are dealing with $(p/p_0)_1$ values uncorrected for deviations from the ideal gas, since such refinements would be totally unjustified. In the text we use the

¹² X_1 is generalized concentration. When the unit mass is the mole, as in equation (3'), $X_1 \equiv N_1$, the mole fraction of component 1.

¹⁸ Equation (3') is obtained by subtracting $RT^2 d \ln p_1/dT = (H'' - H'')_0$, for the pure volatile component from the corresponding expression for the three phase S—L—V pressure (compare e.g. Commentary on the Scientific Writings of J. Willard Gibbs, Yale University Press, New Haven, vol. 1, article by Morey, p. 243, equation 8), suitably rearranged in terms of $RT = pV''$, $H = ST$ ($\equiv \eta t$ of Gibbs) and neglecting the volume per mole of the condensed phases in comparison with that of the vapor phase.

symbol for the activity, a_1 in place of the vapor pressure ratio, as an abbreviation. The concentration is expressed in mole fractions of H_2O and B_2O_3 as components.

The older literature on the subject is summarized to 1924 in Mellor's Treatise,¹⁴ and to 1926 in Gmelin's Handbuch.¹⁵ Since 1926 work has been done by Gilbert and Levi,¹⁶ Bezzi,¹⁷ Menzel, Schulz and Deckert,¹⁸ Thiel and Siebenbeck,¹⁹ and by von Stackelberg, Quatram and Dressel.²⁰ The latter sketched in an approximate P—T diagram for parts of the system.

The pressure-composition (P—X) relations in this system are typical of many aqueous solutions of inorganic substances, exhibiting relatively high negative deviations from Raoult's law at high concentrations of the solute. At the aqueous end the a_1 — N_1 curve starts out with a slope of 2, which is equivalent to Raoult's law being valid when the concentration is expressed in terms of H_2O and H_3BO_3 as components. In this region, measurements have been made by Tammann, Gerlach, Kahlenberg, Skirrow, and others, up to the composition of the saturated solution at the normal boiling point. For higher concentrations, there are available no direct measurements of the vapor pressures of solutions of accurately known compositions. We have made use of the three phase (S_I — S_{II} —V) pressure data of Gilbert and Levi, Lescoeur, Bezzi, Menzel and coworkers, and Thiel and Siebenbeck for the dissociation of orthoboric acid to metaboric acid and water vapor, in combination with the location of the corresponding quadruple points from the solubility data.

These three phase pressure data fall on two separate curves. Bezzi's results must be for dissociation to HBO_2 . They can be represented with good approximation by the Nernst type equation

$$(4) \quad \log p_{mm} = \frac{-12350}{4.574T} + 1.75 \log T + 4.8115,$$

¹⁴ A Comprehensive Treatise on Inorganic and Theoretical Chemistry, by J. W. Mellor: Longmans Green and Co., London and New York, vol. 5, 1924.

¹⁵ Gmelin's Handbuch der anorganischen Chemie, 8. Auflage, Verlag Chemie, Leipzig and Berlin, System Nummer 13, 1926.

¹⁶ Gilbert and Levi: J. Chem. Soc., 527, 1929.

¹⁷ Bezzi, S.: Gazz. chim. ital., 65, 766, 1935.

¹⁸ Menzel, Schulz and Deckert: Z. anorg. allgem. Chem., 220, 49, 1934.

¹⁹ Thiel and Siebenbeck: Z. anorg. allgem. Chem., 220, 236, 1934.

²⁰ Von Stackelberg, Quatram and Dressel: Z. Elektrochem., 43, 14, 1937.

which yields for the heat of dissociation (with the evolution of water vapor) the value

$$(4') \quad \Delta H_{DII} = 12350 + 3.475 T.$$

The eutectic composition for the coexistence of H_3BO_3 and HBO_2II ($169.6^\circ C.$) combined with equation (4) yields

$$(4'') \quad a_1 = 0.373, N_1 = 0.707 (N_2 = 0.293).$$

The measurements of Gilbert and Levi (their series I), Lescoeur, and of Menzel and coworkers must represent the dissociation of H_3BO_3 to form HBO_2III , and yield the equations

$$(5) \quad \log p_{mm} = \frac{-13940}{4.574T} + 2 \log T + 4.8254,$$

$$(5') \quad \Delta H_{DIII} = 13940 + 3.972 T,$$

which combined with the location of the eutectic for H_3BO_3 and HBO_2III ($158.5^\circ C.$) yields

$$(5'') \quad a_1 = 0.242, N_1 = 0.620 (N_2 = 0.380).^{21, 22}$$

Gilbert and Levi's series II will be referred to at a later place. Their series III to IX obviously represent data for unsaturated solutions, but it is not clear what the exact compositions were. Their own explanation of these results in terms of various polyboric acids is untenable, but the data are of value in indicating, at least roughly, the course of the a_1-N_1 curve in the region of high B_2O_3 concentrations.

²¹ The coefficient of $\log T$ in (5) was made equal to 2 in round numbers to bring the values of the vapor pressure constant in equations (4) and (5) to approximately the same value.

²² It is of interest to note that the transformation of HBO_2III to HBO_2II must have occurred during Thiel and Siebenbeck's measurement of the dissociation pressure at $100^\circ C.$ They remark: "Charakteristisch ist die ausserordentliche Langsamkeit, mit der sich das Gleichgewicht uber reiner Orthoborsaeure als Ausgangssubstanz ausbildet. Noch nach 120 Stunden Versuchsdauer ist der stabile Endwert nicht erreicht." From their context it is evident that the pressure was rising, as it should in the case of the above-mentioned transformation. The sluggishness of the process could only be due to the slowness of the conversion rather than to any necessary lack of equilibrium of the vapor with the solids present, since neither Bezzi, nor Gilbert and Levi nor Lescoeur had any pronounced difficulties in establishing equilibria.

The derived pressure-composition relations are represented in Fig. 2, by plotting $(p/p_0)_1 = a_1$ against the concentration N_1 of water in mole fractions of H_2O and B_2O_3 . By trial it was found that a useful deviation curve could be constructed by plotting $a_1^{1/3}$ against N_1 .

At the aqueous end, as already stated, the solutions approxi-

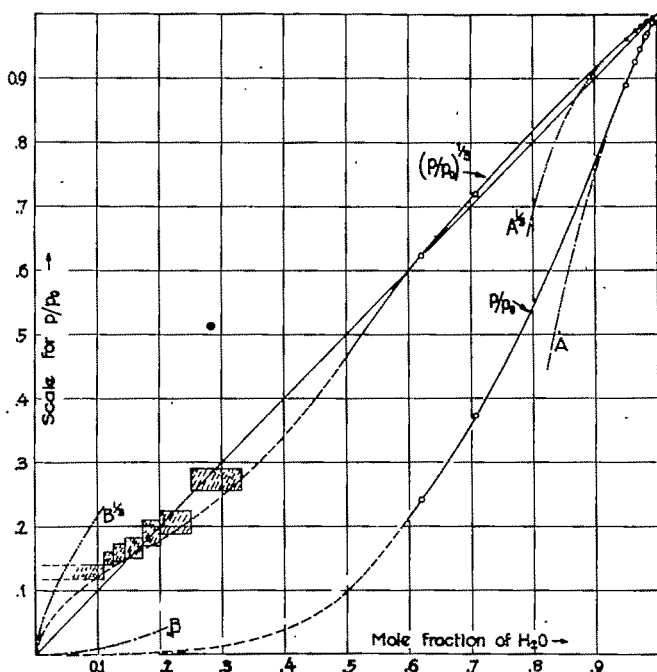


Fig. 2. Relative vapor pressure and composition relations for $H_2O - B_2O_3$ solutions. For explanation consult the text.

mately obey Raoult's law for $H_2O - H_3BO_3$. Curves A and $A^{1/3}$ represent the expected course of the curves on this basis.

At the B_2O_3 end we have assumed that the $a_1 - N_1$ curve starts out in accord with Raoult's law for HBO_2 and B_2O_3 as components, on the basis that the melting curve of crystalline B_2O_3 (vide supra) yields a straight line of $\log N_2'$ against $1/T$. Curves B and $B^{1/3}$ represent the expected course of the curves on this basis, which requires that a_1 be proportional to N_1^2 . Actually, at the present state of our knowledge of the vapor pressure relations, the point is of minor importance in our cal-

Menzel and coworkers measured the vapor pressures of saturated solutions of H_3BO_3 at 13.5°, 15° and 17.5° C., obtaining 11.4, 12.6 and 14.8 mm. Hg. The calculated values at these temperatures are 11.48, 12.65 and 14.80 mm. Hg., the solubilities being 0.58, 0.61 and 0.66 mole per cent B_2O_3 , respectively. The calculated curve is accurate by construction at the boiling

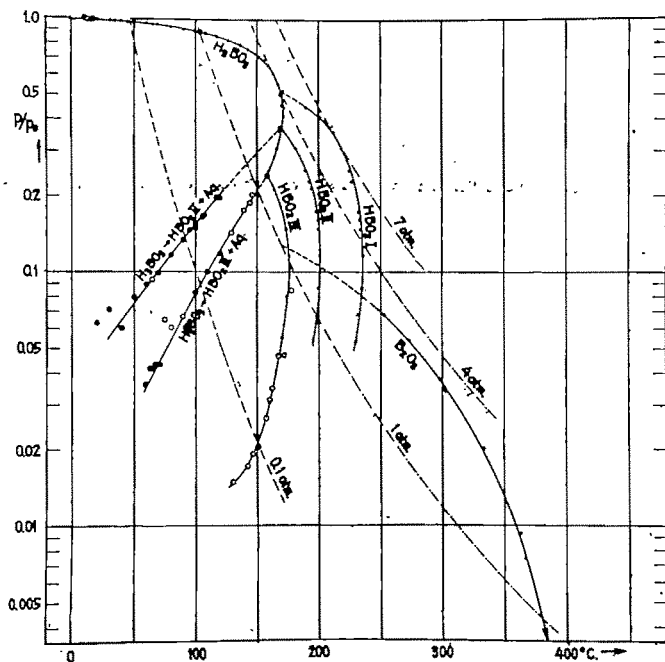


Fig. 4. Relative vapor pressure and temperature relations for the saturated solutions in the system, $\text{H}_2\text{O} - \text{B}_2\text{O}_3$. Experimental points are marked same as in Fig. 3.

point of the saturated solution, 103.2° C. The solubility at this point is 4.86 mole per cent B_2O_3 .

Von Stackelberg and collaborators measured roughly the vapor pressure for melting H_3BO_3 at 170° C., 4.0 atm. ($a_1 = 0.51$), for melting HBO_2 at 203° C., 2.9 atm. ($a_1 = 0.18$), and for a composition given as 2g. H_3BO_3 , 1g. HBO_2 (equivalent to 31.5 mole per cent B_2O_3), 168° to < 190° C., 3.9 atm. The calculated value of a_1 at 25.0 mole per cent B_2O_3 , the composition of H_3BO_3 , is 0.448 (see Tables I and II) as compared with the above measured value of 0.51. Actually the liquidus

curve for H_3BO_3 passes through $a_1 = 0.51$ at approximately 169.7°C. , the corresponding composition of the solution being about 22.0 mole per cent B_2O_3 . When we remember that this is a dissociating compound²³ and that any solution that will be first formed will tend to be an unsaturated solution, the agreement is all that could be desired. In the case of the second point measured by these investigators, the agreement is not quite so fortunate. The calculated value of a_1 at the composition HBO_2 is 0.101, as against their reported value 0.18, which would correspond to a solution of about 43 mole per cent B_2O_3 . The measurement was made at 203°C. , which is above our melting point of HBO_2II , which obviously was the phase present. However, it must be pointed out that this phase requires a considerable time to come to equilibrium with its solutions, and it is to be expected that the first solution formed will be a water-rich solution rather than otherwise, for the same reason that was advanced in the case of H_3BO_3 . The method employed was an ingenious one, but there is some question whether sufficient time was given to reach equilibrium. Thus, in the case of the third point reported by these workers, the pressure could not have remained fixed over the reported range of temperature if the composition given is accurate. The liquidus for HBO_2II at the given composition is 176°C. , calculated $a_1 = 0.335$, which yields 3.02 atm. at the liquidus. Beyond this temperature the solution would be unsaturated, and would exert the reported vapor pressure of 3.9 atm. at just above 187°C. Their upper temperature, $< 190^\circ \text{C.}$, may have been near this value.

The last measurements to be considered as a check on the calculations are those of series II of Gilbert and Levi. Reference to Figs. 3 and 4. shows that the average curve through their experimental points forms a continuation of the calculated curve for HBO_2III . The measured and the calculated portions of this curve agree to within ± 0.5 per cent in the activity values. It should be mentioned that the measurements of this series were not, and could not be, used in establishing the pressure-composition relations, since the composition of the solution was variable, owing to the presence of the solid phase. From the correlation it would appear that the composition in the apparatus must have been just over 50 mole per cent B_2O_3 .

²³ See for example, F. E. C. Scheffer, *Z. physik. Chem.* 71, 214, 671, 1910; A. Smits, *ibid.* 67, 455, 1909.

Since we have made the explicit assumption of von Babo's law in these calculations, it must be expected that in certain regions of the diagram the calculated $P - T - X$ relations will be somewhat inaccurate. Another source of error lies in neglecting the contribution to the vapor pressure due to the presence of boric acids in the vapor phase. The error due to this factor is, however, of secondary importance. The calculated diagram is correct in principle, and as we have seen, in moderately good numerical agreement with fact throughout the relatively enormous region of compositions described.

It will be noted that the vapor pressures of solutions saturated with the various phases pass through maxima, located in each case on the H_2O side of the composition of the phase in question. The most interesting feature is that crystalline B_2O_3 can exist in equilibrium with solutions which exert a considerable vapor pressure. The vapor pressure maximum is located at about $280^\circ C.$, being somewhat less than 3 atm. The corresponding composition of the saturated solution is about 62 mole per cent B_2O_3 . It will be recalled that in many of the recorded unsuccessful attempts to crystallize this compound, the work was done on the anhydrous vitreous oxide, a region of composition which is particularly unsuitable for accomplishing the desired end. Another interesting point which arises in connection with the vapor pressure relations is that as the composition approaches 100 per cent B_2O_3 , the aqueous pressures decrease to very low values (compare Fig. 2). This explains the observed difficulty of completely dehydrating the substance at moderate temperatures.

The Liquid-Vapor Composition Relations.

The experimental data now available on the volatility of boric acid from its solutions cover a comparatively narrow range of compositions, extending only up to the saturated solution at the normal boiling point. It is planned to extend this range by working at higher temperatures; in the meantime, it seems worth while to review the data already available.

The results of von Stackelberg and coworkers, on recalculation to mole fractions of H_2O and B_2O_3 , may be expressed by

$$(6) \quad \left(\frac{N_1}{N_2} \right)_{\text{vapor}} = (280 \pm 20) \left(\frac{N_1}{N_2} \right)_{\text{liquid}}$$

while those of Bezzi (and Skirrow) depart rather widely from the above, being best expressed by

$$(7) \quad \left(\frac{N_1}{N_2} \right)_{\text{vapor}} = 550 \left(\frac{N_1}{N_2} \right)_{\text{liquid}}^{0.63}$$

over approximately the same range of composition.

The data of von Stackelberg et al. on the volatility of crystalline H_3BO_3 and HBO_2 in steam lead to the view that as the concentration of B_2O_3 greatly increases in the solution, the distribution coefficient will change in the direction in which the vapor will be relatively impoverished in B_2O_3 . This is to be expected also on the basis of our limited knowledge of the volatility of vitreous B_2O_3 . Accordingly, the distribution coefficient in equation (6) should rise with increasing concentration of B_2O_3 in solution.

A further numerical discussion of this question at this time would serve no useful purpose. The problem is of some importance in volcanology, and especially, in the study of the origin of the vapors rich in boric acid, which arise from steam vents and from steam wells in the hot spring regions of Italy, and elsewhere.

PROPERTIES OF THE CRYSTALLINE PHASES.

We have measured the density, the optical, and the crystallographic properties of all the new compounds prepared in this study, with the exception of the crystallographic properties of crystalline B_2O_3 , which could be prepared only in microscopic crystals. We have also taken the opportunity to add to the known observations on H_3BO_3 (sassolite).

Sassolite, H_3BO_3 , has been described by several observers. Further details of twinning, cleavage, flexibility, and optical properties of artificial crystals are presented here.

Microscopically, the triclinic crystals are tables with six 120° angles, bounded by $a\{100\}$, $p\{110\}$, $q\{1\bar{1}0\}$ of Haushofer's orientation, or prisms with the axis oblique to the base 15° . Besides the eminent basal cleavage, a poor cleavage develops parallel to the a -axis when basal plates are flexed repeatedly about that axis. Resistance to such flexing is decided, but about the b -axis the plates flex with extreme ease, while a set of twinning lamellae develops, which outcrops on the base at an angle of $10^\circ \pm 2^\circ$ to the b -axis and of $50^\circ \pm 2^\circ$ to p . Many

prismatic crystals of megascopic size were found twinned according to the albite law, with the twinning and composition plane $b\{010\}$.

Microscopically extinctions are nearly parallel to the base (see below) and in the prism zone the maximum extinction angle, that is, $a \wedge c$, is 16° .

On the base the optic axial plane makes an angle of $17^\circ \pm 2^\circ$ with $a\{100\}$ and of $43^\circ \pm 2^\circ$ with $q\{1\bar{1}0\}$, and from measurements on the interference figures the acute bisectrix, a , is inclined 2° from the normal to the base toward $p\{110\}$. $-2V = 10^\circ$, $-2E = 15^\circ$. The refractive indices are $a = 1.337$, $\beta = 1.461$, $\gamma = 1.462$.

Metaboric Acid HBO_2 III. The crystals examined for optical and crystallographic properties were grown by deposition from the vapor phase: orthorhombic prism and base; tabular parallel to the base, or stubby prisms; interior prism angle measured microscopically $78\frac{1}{2}^\circ$. No better value was obtained goniometrically from the best available crystals with hydrated surfaces. Cleavage is so easy, parallel to the base, that slight pressure causes shearing of a crystal into many thin flakes. The optic axial plane bisects the acute angle of the prism. $-2V = 23^\circ$ without noticeable dispersion, and with a , the acute bisectrix, normal to the base. Refractive indices are $\gamma = 1.521$, $\beta = 1.514$, a , in hexane, is less than 1.376. The crystals react rapidly with acetone, methyl alcohol, and acetonitrile.

The density was measured on crystals prepared in sealed tubes by quenching melted HBO_2 and recrystallizing the glass at 160° C. for 2 hours. The material was microcrystalline, but contained no HBO_2 II or HBO_2 I. The value obtained, 1.78, was measured in a pycnometer with toluene as the displacement liquid, after evacuation to remove the air.

Metaboric Acid HBO_2 II. The holohedral monoclinic crystals from the vapor have a slightly elongated lenticular aspect, with the broad bulging front pinacoid rounded by two pyramids and a dome, to a small base. A very perfect basal cleavage meets a less perfect orthodomal cleavage $\{\bar{1}01\}$ at an interior angle of $86\frac{1}{2}^\circ$. The optic axial plane is $\{010\}$; $\gamma \wedge c$ -axis = 5_r° , $4\frac{1}{2}_b^\circ$ in acute angle β ; $-2V = 35_r^\circ$, and 36_b° . The refractive indices $a = 1.434$, $\beta = 1.570$, $\gamma = 1.588$; and the axial ratios $a:b:c = 0.81:1:1.78$, have been obtained as preliminary values on rough crystals with surfaces slightly altered

by hydration. The observed angles, according to two-circle goniometry, are:

Forms		ϕ	ρ
<i>c</i>	001	90°	30½°
<i>d</i>	111	60	74½
<i>e</i>	012	35½	47½
<i>g</i>	111	48	69

The density, measured in a pycnometer on coarsely crystalline material resulting from dehydration of H_3BO_3 at 130° C. was 2.044 ± 0.003 . The composition of the crystals was 79.40 ± 0.05 per cent B_2O_3 .

Metaboric Acid HBO_2 I. The most stable form of metaboric acid crystallizes as rhombic dodecahedra, and has the refractive index 1.619.

The density was measured both by flotation in a heavy liquid and in a pycnometer. The results agree closely, being 2.487 and 2.485, respectively, each ± 0.003 . The crystals were grown in sealed tubes.

Crystalline Boron Oxide, B_2O_3 . The largest crystals (diameter about 0.05 mm.), prepared by crystallization in solution in a sealed tube for about eight months, had the aspect of rhombohedra, and each contained a nucleus of a dodecahedral crystal of metaboric acid HBO_2 I. Marked parallelism between the edges—and probably the faces—of the two were seen, but no definite crystallographic relationship could be established, because strain birefringence, and other irregularities in refractive index obscured the optical relationships. However, the crystals are nearly or quite uniaxial, with ω (or β and γ) = 1.64₈ and ϵ (or α) = 1.61₅. Crushing either induces a minute lamellar twinning, or possibly reveals a twinning caused by an inversion.

Crystals of B_2O_3 , which are grown only a short time in solution, or produced by crystallization of the melt, are very minute. For measurement of the density, the crystals were prepared by crystallizing a seeded melt. The composition was 100 ± 0.1 per cent B_2O_3 . The density is 2.460 ± 0.010 , measured in a pycnometer.

The powder diffraction pattern for crystalline B_2O_3 was obtained for us by C. J. Ksanda of this Laboratory. This pattern was found to be in good agreement with that reported by McCulloch, but different from that of Cole and Taylor.

The determination of the crystal structures of the new

crystalline phases has been kindly undertaken by W. H. Zachariasen, who will report his findings separately elsewhere. We are privileged to state at this time that his results agree with ours on the symmetry of HBO_2I and HBO_2II , as follows:

The structure of HBO_2I is cubic, $a_0 = 8.87_9 \text{ \AA}$ with an accuracy of 0.1 per cent. This, combined with the density value of 2.486 yields 24 molecules of HBO_2 per unit cell.

The monoclinic unit cell of HBO_2II has the dimensions $a = 7.12 \text{ \AA}$, $b = 8.86 \text{ \AA}$, $c = 6.85 \text{ \AA}$, angle $\beta = 93^\circ 30'$. The axial ratios $a:b:c$ are $0.803_6:1:0.773_1$, as contrasted with the crystallographic (*vide supra*). The X-ray cell transformed to the crystallographic orientation yields $a:b:c = 0.803_6:1:1.785$, angle $\beta = 59^\circ 48'$. There are 12 molecules of HBO_2 per unit cell, and the space group is probably C_{2h}^5 .

DISCUSSION.

In the preceding pages we have already discussed the equilibrium relations between the various phases in some detail, and have pointed out some of the more important features of this investigation, together with its bearing on the work of this Laboratory. It remains to mention some of the problems which remain to be studied, and some conclusions that may further be drawn from the work already completed.

It should be emphasized that B_2O_3 is a unique substance. In its vitreous form it is tough rather than brittle, and this property appears to be carried over into the crystalline form, the scratch hardness of which is certainly below that of steel, but which resists crushing to an extraordinary degree. The thermal properties of B_2O_3 have been studied in considerable detail in the form of glass by G. S. Parks, W. E. S. Turner and others, but the thermal properties of the crystals still remain to be investigated. The fact that both the melting point and the softening point are relatively low on the temperature scale makes it an ideal substance to be studied from this point of view. An X-ray study of the constitution of the glass has been made by B. E. Warren, and has led to conclusions which are in essential agreement with those arrived at by W. H. Zachariasen on more qualitative grounds. The X-ray study of the structure of the crystals has been begun.

In studying the solubilities, all the crystalline phases, except ice, have been observed to sink in the coexistent solutions; for these denser phases, the immediate effect of increasing pres-

tures is to raise the melting temperatures. For B_2O_3 a very rough estimate of the rise is 3° per 100 atmospheres, made by neglecting the effect of compressibility, and by assuming (1) that the latent heat of melting is of the order above calculated, (2) that the thermal expansion of the crystals is about the same as that of the glass. For ice, the melting temperature is first lowered at the rate of 1° per 100 atmospheres increase of pressure, but beyond 2000 atmospheres, the melting temperature also begins to rise.

Many other problems could be discussed here. We shall confine ourselves to pointing out that the volatility relations in this system are of special interest, differing from those usually encountered in that both components are volatile within the system, although B_2O_3 itself is practically nonvolatile in the complete absence of water. Within the system, the B_2O_3 content of the vapor must be ascribed to the formation of compounds stable in the vapor phase. The system is not unique in this respect, but very little is known in the literature concerning such behavior.

ACKNOWLEDGMENT.

The authors are particularly indebted to their colleague C. J. Ksanda, and to Prof. W. H. Zachariasen of the University of Chicago for their contributions to this investigation.

SUMMARY.

The equilibrium diagram for the system of water and boron oxide has been established by measuring the solubility over the whole range of compositions.

The crystalline phases which occur in the system are ice, H_3BO_3 , three modifications of HBO_2 , which are monotropically related to each other, and crystalline B_2O_3 . Solubility relations have been determined for each of these phases.

The solubility curve for ice extends only from the melting point of ice to the cryohydric point at $-0.76^\circ C$. The curve for H_3BO_3 rises smoothly from this point to a maximum at the melting point (metastable) of H_3BO_3 , $170.9^\circ C$., and then descends to end at the metastable eutectic for HBO_2 III and H_3BO_3 .

The three forms of HBO_2 melt congruently, HBO_2 I, the stable modification, at $236^\circ C$., and HBO_2 II and HBO_2 III, both metastable, at $200.9^\circ C$. and $176.0^\circ C$., respectively.

Their solubility curves have flat maxima at the composition HBO_2 . The curve for the stable form, HBO_2I , intersects the curve for H_3BO_3 at 169°C ., at which point H_3BO_3 decomposes to form HBO_2I and a solution of the equilibrium composition. The reaction is an abnormally sluggish one, so that the metastable continuation of the solubility curve of H_3BO_3 is realized as if HBO_2I did not exist. The curves for HBO_2II and HBO_2III intersect that of H_3BO_3 at metastable eutectics located at 169.6°C . and 158.5°C ., in the order given.

Crystalline B_2O_3 melts at $450^\circ \pm 2^\circ \text{C}$. It has been crystallized from solution in sealed tubes, as well as in open vessels at atmospheric pressure, and various factors influencing its spontaneous growth have been established. The solubility curve for B_2O_3 extends from the melting point to the intersection with the curve of HBO_2I at 235°C ., and with that of HBO_2II at 200°C . Both of these points are eutectics, the second being metastable.

P—T—X relations for the saturated solutions have been evaluated by combining the solubility data with deductions based on existing vapor pressure measurements. The resulting diagram, described in the text, brings out, among other things, the interesting fact that crystalline B_2O_3 can coexist with solutions at a vapor pressure of about 3 atmospheres in the neighborhood of 280°C . The oxide crystallizes relatively rapidly in sealed tubes in this region of temperature. The oxide crystallizes exceedingly slowly, on the other hand, from the nearly anhydrous melts of vitreous B_2O_3 , and never spontaneously, in this region of composition. The spontaneous crystallization is initiated, in the more aqueous solutions, by the presence of HBO_2I , but not by the presence of the other modifications of metaboric acid.

The crystallographic and optical properties of the new crystal phases were measured, and are described in detail in the text.

THE UNIT CELL AND SPACE-GROUP OF β -GLYCINE.

C. J. KSANDA AND G. TUNELL.

ABSTRACT.

The dimensions of the structural unit cell of β -glycine, all determined by purely röntgenographic measurements, are $a_0 = 5.07 \text{ \AA}$, $b_0 = 6.23 \text{ \AA}$, $c_0 = 5.37 \text{ \AA}$, all $\pm 0.01 \text{ \AA}$, $\beta = 113^\circ 27' \pm 15'$. β -glycine crystallizes either in the space-group $C_{2h}^2 - P2_1/m$ or in the space-group $C_s^2 - P2_1$.

Faceted crystals of β -glycine were investigated by means of the Weissenberg X-ray goniometer,¹ and the reflection goniometer. The crystals were prepared by dissolving 1 gram of glycine in 10 cc. of distilled water, cooling the solution in ice, and adding 20 cc. of cooled 96 per cent ethyl alcohol slowly and with stirring. Acicular crystals precipitated which were freed from the solution in a sintered silica filter under partial vacuum and dried quickly in an evacuated desiccator. The β -form inverts to the α -form in air but can be preserved for some time in an evacuated desiccator. Representative crystals of β -glycine are shown in Fig. 1. It was found that the use of more concentrated aqueous solutions caused precipitation of the α -form with the β -form.

The crystals of β -glycine selected for X-ray investigation by the equi-inclination method were elongated parallel to the b -axis and almost equi-dimensional in cross-section (about 0.1 mm. in diameter). After the exposure of the Weissenberg photographs, the crystals were placed under the polarizing microscope in an immersion liquid, and proved not to have inverted to the α -form. A rotation photograph was taken with the crystal rotating around the b -axis, and Weissenberg resolutions were made of the equator and first layer-line, also a rotation photograph and an equator Weissenberg resolution about the a -axis. The dimensions of the monoclinic unit cell, all determined by purely röntgenographic measurements, are $a_0 = 5.07 \text{ \AA}$, $b_0 = 6.23 \text{ \AA}$, $c_0 = 5.37 \text{ \AA}$, all $\pm 0.01 \text{ \AA}$, $\beta = 113^\circ 27' \pm 15'$. The axial ratio calculated from the unit cell dimen-

¹ The X-ray study of β -glycine was suggested to the authors by Mr. L. H. Adams in connection with some compressibility measurements carried out by him.

sions is $a:b:c = 0.814:1:0.862$. The angles between the faces in the prismatic zone (parallel to the b -axis) were also measured on a reflection goniometer and the value of β was found to be $113^\circ 22' \pm 5'$, in good agreement with the X-ray determination. A comparison of the unit cell dimensions determined by the authors with those determined by Bernal is given in Table I.

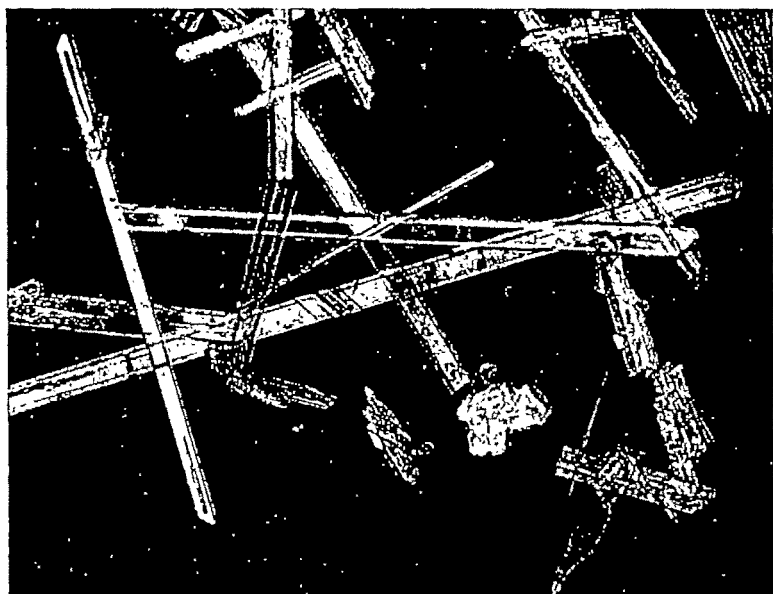


Fig. 1. Faceted crystals of β -glycine. Crossed nicols. 100 \times .

The Weissenberg photographs were indexed by the graphical construction of Schneider.² According to a preliminary report on *The crystal structure of the natural amino acids and related compounds* by J. D. Bernal,³ β -glycine crystallizes in the space-group C_s^{2n} , but this is not correct, since there are no systematic absences of spectra from (*hol*) planes. Comparison of the Weissenberg photographs of the equator and first layer-lines taken with the crystal rotating around the b -axis shows that the lattice is primitive and without glide planes.

² Z. Krist., 69, 41-48, 1928.

³ Z. Krist., 78, 363-369, 1931.

The b -axis appears to be a screw axis, since the odd orders from the clino-pinacoid were absent on the equator Weissen-

TABLE I.
Comparison of the Dimensions of the Structural Cells of
 β - and α -Glycine.

		a_0	b_0	c_0	β
β -glycine	Ksanda and Tunell	5.07	6.23	5.37	$113^\circ 27'$
	Bernal	5.18	6.18	5.29	$114^\circ 20'$
α -glycine	Ksanda and Tunell	5.06	11.93	5.43	$111^\circ 29'$
	Bernal	5.04	12.1	5.41	$111^\circ 38' \dagger$
	Hengstenberg and Lenel*	5.1	11.9	5.43	$111^\circ 38' \dagger$

* Z. Krist., 77, 424-436, 1931.

\dagger The value of the β -angle was taken by Hengstenberg and Lenel from the literature; the same value appears in Bernal's table.

berg photograph taken with the crystal rotating around the α -axis. The space-group of β -glycine is accordingly either $C_{2h}^2-P2_1/m$ or $C_2^2-P2_1$, the characteristically missing spectra of these two space-groups being the same. The crystals were tested for a piezo-electric effect,⁴ but none could be detected; the question as to the crystal class of β -glycine therefore cannot be answered definitely without further evidence.

The density calculated from the unit cell dimensions on the assumption that the cell contains 2 molecules of $\text{CH}_2(\text{NH}_2)\text{COOH}$ is 1.592. The calculated value agrees sufficiently well with unpublished measurements of the density, made in the Geophysical Laboratory by L. H. Adams and R. E. Gibson, to establish the number of molecules in the unit cell as two.

In order to facilitate the future identification of β -glycine by the powder method, the planar spacings and relative intensities of the diffraction lines in a powder photograph of β -glycine taken with Cu-radiation filtered through nickel foil are assem-

⁴ The authors are indebted to Messrs. S. B. Hendricks and M. E. Jefferson of the U. S. Department of Agriculture, Bureau of Chemistry and Soils, for their kindness in making this test.

TABLE II.

Planar spacings and relative intensities of diffraction lines of powder spectra of β - and α -glycine taken with Cu-K radiation filtered through nickel foil. Powder specimens were rotated uniformly during the exposure. Estimated intensities of the diffraction lines are based on a scale of ten, where ten represents the intensity of the strongest line in each case.

Line No.	β -form			α -form		
	Intensity estimated	d/n	hkl	Intensity estimated	d/n	hkl
1	10	4.912	001	3	5.960	020
2	1	4.640	100	7	4.689	100
3	2	4.360	101	4	4.415	110, 101
4	9	3.773	110	2	4.129	111
5	7	3.115	020	8	3.696	120
6	6	2.871	101	5	3.129	031
7	5	2.656	102, 021	4	3.043	130
8	8	2.454	112	10	2.974	040
9	5	2.302	200, 012	7	2.520	002, 140
10	5	2.194	210, 202	8	2.450	141, 211
11	3	2.057	212	2	2.363	131
12	2	1.969	221	3	2.327	200
13	3	1.899	102, 130	2	2.212	132
14	2	1.853	220	3	2.139	202, 051
15	6	1.722	113	2	2.098	150, 212
16	4	1.643	003, 213	4	2.040	151, 141
17	6	1.593	231, 032	2	1.995	230, 222
18	1	1.561	040	4	1.927	102, 241
19	2	1.514	310, 232	4	1.908	112
20	2	1.492	223	3	1.857	232

TABLE II.—Continued.

21	2	1.450	023,	322,	303	5	1.793	221,	161		
22	3	1.407	313	141		2	1.742	132			
23	6	1.358	113,			2	1.705	251,	242		
24	2	1.332	104,	204		1	1.650	250,	213		
25	1	1.304	114,	214		6	1.625	161,	133		
26	2	1.253	401,	402		3	1.603	071,	302		
27	2	1.235	004,	330,	304,	3	1.567	300,	171		
28	5	1.210	051,	014,	314	4	1.521	260,	320		
29	1	1.194	151,	403		1	1.491	080,	332		
30	1	1.183	333			4	1.471	171,	251,		
31	3	1.169	400,	422,		1	1.440	153,	172		
32	2	1.151	133,	203		4	1.422	313,	081,		
33	1	1.127	152,	213,	302	2	1.386	323	342		
34	1	1.113	052,	312		3	1.348	333			
35	3	1.093	250,	340		1	1.323	204,	181		
36	6	1.076	114,	404,	252	1	1.316	242			
37	2	1.064	322,	343		1	1.288	331			
38	1	1.030	124,	411		2	1.269	134			
39	1	1.003	233,	502,	253	6	1.233	360,			
40		4	1.181	400,	304,	353,	282
41		1	1.158	302,	0 10 0,	351,	262
42		2	1.134	322	420,	254,	0 10 1
43		1	1.120	104			
44		3	1.107	272,	283,	083	
45		1	1.085	373,	1 10 2		
46		2	1.071	404,	134,	342,	2 10 1
47		1	1.060	371,	215,		
48		2	1.049	274,	193,	462,	1 11 0
49		1	1.025	183	461,		
50		1	1.017	471,	472,	381,	1 10 2

bled in Table II. The lines were indexed by an application of Bernal's graphical method in which all possible spacings in the β -glycine structure down to $d/n = 1.000 \text{ \AA}$ were taken account of. The β -form when freshly crystallized has a great tendency to invert to the α -form, and in order to obtain a powder photograph of β -glycine unmixed with α -glycine care must be taken to remove all adsorbed water from the surface of the β -glycine. The crystals should be thoroughly washed with alcohol and immediately placed in a desiccator over phosphorus pentoxide and the desiccator evacuated with a vacuum oil pump in order to remove the last traces of moisture from the crystals. The crystals grown for the powder spectrum

TABLE III.
The Optical Properties of β - and α -glycine.*

	Optical character	α	β	γ
β -glycine	Biaxial (—)	1.490	1.608	1.652
α -glycine	Biaxial (—)	1.502 •	1.618	1.670

* Determined by N. L. Bowen.

were exceedingly small, prepared by quick precipitation; they were thoroughly dried and without grinding were mounted on a fine thread of Pyrex glass by means of a film of vacuum grease. The specimen was rotated uniformly during the exposure.

Rotation, Weissenberg, and powder photographs were also taken of crystals of α -glycine for the purpose of comparison. The values found for the dimensions of the monoclinic structural cell of α -glycine, all obtained by purely röntgenographic measurements, are $a_0 = 5.06 \text{ \AA}$, $b_0 = 11.93 \text{ \AA}$, $c_0 = 5.43 \text{ \AA}$, all $\pm 0.01 \text{ \AA}$, $\beta = 111^\circ 29' \pm 15'$. The axial ratio calculated from the unit cell dimensions is $a:b:c = 0.424:1:0.455$. The planar spacings and relative intensities of the diffraction lines in a powder photograph of α -glycine taken with Cu-radiation filtered through nickel foil are assembled in Table II. The lines were indexed by an application of Bernal's graphical method in which all possible spacings in the α -glycine structure down to $d/n = 1.000 \text{ \AA}$ were taken account of. A comparison of the values of the unit cell dimensions determined by the authors and previous investigators is given in Table I.

The optical properties of β - and α -glycine have been determined by means of the immersion method by Dr. N. L. Bowen and are collected in Table III.

CLAYS AND OTHER MINERALS FROM THE DEEP SEA, HOT SPRINGS, AND WEATHERED ROCKS.

H. E. MERWIN AND E. FOSNJAK.

ABSTRACT.

X-rays and optical methods were used. Comparison materials, especially clays, required study. It was found desirable in the nomenclature of the optical properties of clays to take account of the differences in aggregate refractive indices observed for most clays when differently immersed. Staining was used to indicate the presence and the character of clays.

Some of the minerals observed in the bottom samples taken by the *Carnegie* were: dolomite, considered syngenetic; muscovite, considered residual; montmorillonite and phillipsite, syngenetic; and one unidentified iron-manganese mineral.

Some constituents of the samples described in this paper were identified petrographically, others by means of X-ray powder patterns.

Deposits may contain dispersed clay which, if the sample is dried, adheres to the larger grains. An informative separation before drying can be made rapidly by taking up a little of the deposit with water in a medicine dropper, then as successively finer portions settle, depositing them as separate droplets on a slide. These may be dried, or the finer portions may be examined wet. The search for clays in deposits is expedited by applying stains, as described below.

CLAYS.

Petrographic Examination of Clays.

The optical properties of some clay minerals appearing in determinative tables are those of indefinite porous aggregates for which a numerical value as obtained by the immersion method may represent a sum or combination of effects due chiefly to the stable part of the clay mineral, and to the immersion liquid which has replaced part of the loosely held water and has partly filled the pores. A symbol is needed to indicate such indefiniteness in case of aggregates of various kinds. *Sigma* might be used as a subscript: $n_{\Sigma} = 1.48$, $n = 1.48_{\Sigma}$, $(\gamma - \beta)_{\Sigma} = 0.03$, etc. The designations *aggregate refractive index* and *aggregate birefringence* for these quantities may be

found acceptable. Such numerical values, although indefinite, are essential for comparative studies, and are being made more definite.

Delayed or non-uniform penetration of immersion liquids into porous aggregates has been a source of much uncertainty.¹ Correns and Mehmel² have used for clays a mixture of quinoline and paraldehyde which gave for montmorillonite a maximum refractive index in about two and a half hours. We have observed that the refractive index of this liquid increases rapidly with exposure on a slide, but a test of the rate of its effect on clays for the first few minutes of immersion was made on several beidellites and montmorillonites in grains only a few microns thick. In all cases the aggregate refractive index of many of the grains exceeded 1.572 in less than two minutes (see below). Kaolinite, halloysite and halloysite-hydrate fall below this. In early determinations,³ when slowly penetrating heavy petroleum or fatty oils were used for immersion, the observed refractive indices of beidellite and montmorillonite were usually much lower than those of kaolinite. Whether or not quinoline and paraldehyde penetrate disproportionally is not known.

Aniline is a most rapidly penetrating single liquid of suitable refractive index for the microscopical study of clays. Around a little heap of montmorillonite powder immersed in it an emulsion of the expelled water was seen to form. A lump thus immersed had its displaced water driven at once to the interior. Then by slow diffusion the water escaped, causing a decrease in aggregate birefringence from four to two orders of interference, and an increase in the aggregate refractive index. Aniline (b. p. 183°) mixed with a little iso-amyl iso-valerate (b. p. 194°) and also the quinoline-paraldehyde mixture were used to test the homogeneity of several compact beidellites and montmorillonites. Thin shavings of the clays developed birefringent streaks parallel to the knife edge. For liquids of refractive index 1.57 there were great differences in the rate of penetration for these clays from different localities, but the quinoline liquid was more quickly effective.

¹ Sosmau, R. B., Hostetter, J. C., and Merwin, H. E.: *J. Wash. Acad. Sci.*, 5, 565, 1915; Johnston, J., Merwin, H. E., and Williamson, E. D.: *This Journal*, 41, 482, 1916; Larsen, E. S., and Wherry, E. T.: *J. Wash. Acad. Sci.*, 7, 179 and 209, 1917.

² Correns, C. W., and Mehmel, M.: *Z. Krist.*, 94, 337, 1936.

³ Shannon, E. V.: *U. S. Nat. Museum Bull.*, 131, 388, 1926; Ross, C. S., and Shannon, E. V.: *J. Am. Ceram. Soc.*, 9, 94, 1926.

The birefringence in water of two of these clays (Nos. 2 and 4 of Table I) was estimated on coherent grains as 0.02_s.

In complex deposits, the clay—and some other porous substances—can be stained by having a little safranine, crystal violet, or malachite green in the immersion liquid. If the grains are tinted at room temperature no significant immediate effect of the dye on refractive index has been observed, but by boiling for two minutes montmorillonite, beidellite, halloysite,⁴ halloysite-hydrate,⁴ and the very fine-grained kaolinite⁴ (impure?), indianite, in aniline or anethole containing sufficient safranine, the aggregate refractive indices were raised 0.02 to 0.03 by the dye.

X-ray Examination of Clays.

Most of our comparisons of X-ray powder spectra were made by having a known and an unknown clay pattern on one film. Beidellites and montmorillonites were all very similar except for slight differences in spacings and a few extraneous lines. There was a general tendency for all spacings of one clay to be shifted in the same direction with respect to another clay. Therefore we list in Table I the clays in the order in which their interplanar spacings increase. This table also describes the occurrence of the specimens.

TABLE I.

Order of Interplanar Spacings of Clays.

1. Hillside Springs specimen. It occurred in a rhyolite altered by hot water in Yellowstone Park (see ref. 7). It is probably a very pure aluminum beidellite.
2. Beidellite from Silver City (Carson District). It contains a little CaO (2.76%)—see ref. 3.
3. Beidellite from "The Geysers."^a It is a green clay containing about 6% Cr₂O₃ and 2% Fe₂O₃, according to a partial analysis of another part of the specimen.
4. Beidellite from Colorado.^b This is a specimen containing about 9% Fe₂O₃, and 3% CaO.
5. Light-colored clay from the deep sea nodule, as described below.
6. Otaylite.^c This is a montmorillonite containing about 8% MgO and 1% CaO, besides 3% Fe₂O₃.
7. Dark clay from the deep sea nodule, as described below.
8. Clays from *Carnegie* samples, Nos. 27, 61, and 80. (See Table II.)
^a Allen, E. T., and Day, A. L.: *Carnegie Inst. Wash. Pub. No. 378*, p. 49, 1927.
^b See Ross and Shannon, ref. 3, and also the first reference under c, below.
^c See X-ray diffraction, Hendricks, S. B., and Fry, W. H.: *Soil Sci.*, 29, 457, 1930; and Lauder milk, J. D., and Woodford, A. O.: *Am. Mineral.*, 19, 260, 1934.

⁴ Samples of the halloysites kindly furnished by Dr. S. B. Hendricks. See *Am. Mineral.*, 23, 295, 1938.

ALTERED PUMICE FROM A DEEP SEA BOTTOM SAMPLE
TAKEN BY THE *Carnegie*.⁵

Cross sections of a black nodule one to two centimeters in diameter, from a bottom sample at 5,396 meters depth 200 miles off the coast of Japan, showed irregular color banding from the black surface through a dark brown zone and a buff zone to a white pumiceous interior.

The refractive index of the isotropic pumice was 1.513, except that the largest inter-bubble fragments had a noticeably lower refractivity at the center, as though increase of refractivity by hydration⁶ had been taking place. Glass gave way irregularly, as if by solution, to secondary products without notable pseudomorphic replacement. Near the center of the nodules, bubble cavities were partly filled with a light-colored, decidedly birefringent, unconsolidated clay. Toward the surface, the clay became less birefringent, browner, and denser. The birefringent elements appeared both felted and spherulitic. The *aggregate refractive index* obtained by immersion in aniline mixtures (from less than 1.58 to greater than 1.63) increased with the color toward the surface. The more consolidated darker material just within the surface below the black crusts was nearly isotropic, often with a concentric or irregular layering, and had an aggregate refractive index much higher than 1.63. X-ray spectrograms of the light and dark portions both showed lines characteristic of montmorillonite and beidellite. The interplanar spacings were smaller for the light portion (see Table I).

The black crust of the nodules less than one millimeter thick was minutely botryoidal and contained, besides the main dark brown constituent, small amounts of quartz and montmorillonite. An X-ray powder photograph showed three strong broad lines regarded as characteristic at 2.43, 1.42, and 1.23 Å. The same lines were obtained from five other sources: (1) solid manganese nodules in *Carnegie* bottom sample No. 79 at a depth of 4,918 meters; (2) minute black particles magnetically concentrated from *Carnegie* bottom sample No. 80, depth of 5,003 meters; (3) a weathered manganiferous travertine collected by

⁵This sample (No. 57) and those described later (see Table II) were kindly placed at our disposal by J. S. Fleming, Director, Department of Terrestrial Magnetism, Carnegie Institution of Washington.

⁶Fresh volcanic glasses containing water have higher refractivity than anhydrous ones of otherwise corresponding composition. Tilley, C. E.: *Mineralog. Mag.*, 19, 294, 1922.

Allen⁷ in Yellowstone Park; (4) a black deposit in Firehole Pool, also collected by Allen⁷ in Yellowstone Park and analyzed chemically; (5) a dark brown coating on grains of manganese carbonate from an open bottle that had been standing on a laboratory shelf for several years. All these materials are essentially oxides of iron and manganese, in part hydrated. Therefore powder patterns of them were compared with those of known minerals⁸ of related composition. The results, however, were negative.

SOME MINERALS IN THE SEA BOTTOM SAMPLES
COLLECTED BY THE *Carnegie*.⁹

One highly calcareous sample (No. 21) was treated with dilute citric acid to remove the shells without decomposing the little dark brown globules that had been observed within them. The residual globules were sensibly isotropic with an *aggregate refractive index* of 1.8. The tiny sample was X-rayed, but no identity with a known substance was established. The approximate positions of the lines are listed here, and the stronger ones are italicized: 4.2, 2.7, 2.45, 2.11, 1.71, 1.50, and 1.42 Å. Microscopically this material appears to be like scattered grains five to fifteen microns in diameter found in red clays of the deep ocean.

Dolomite was found in separate microscopic rhombohedra in the following bottom samples: Nos. 29, 62, 64, 65, and 85, from widely separated localities in the Pacific. It would seem not a long step to syngenetic dolomites by direct sedimentation.

In a very fine mud in mid-ocean west of Mexico (sample No. 77), the largest grains were flakes resembling muscovite. By means of X-rays, *muscovite*, *quartz*, and *phillipsite* were found. Derivation from the granitic and metamorphic rocks of western North America is inferred.

Phillipsite, as single or grouped prisms, is often obscured by adherent mud, but it has long been known as a constituent of deep sea deposits. Its birefringence may be very weak even in large zoned crystals. The refractive index is slightly variable

⁷ Allen, E. T., and Day, A. L.: Hot Springs of the Yellowstone Park, Carnegie Inst. Wash. Pub. No. 466, pp. 346, 348, 1935.

⁸ Furnished by the U. S. National Museum through the kindness of Dr. W. F. Foshag. Polionite, R. 2096, and pyrolusite, 86237 (both gave patterns like synthetic MnO₂): psilomelane, 93687; manganite, 82428; braunite, 45375; pyrochroite, R. 2208.

⁹ Minerals not mentioned should not be considered absent. See Table II for locations.

(around 1.495). Outlines of grains may be seen in samples of undried mud taken from filter paper to aniline or quinoline.

Montmorillonite with large interplanar spacings like those of the dark clay of the black nodule was found by X-rays in Nos. 27, 61, and 80. Quartz also was present, and phillipsite in Nos. 27 and 61.

A BOEHMITE SOIL.

A "red" residual soil was collected by T. W. Vaughan from the limestone of the Anguilla formation on the Island of Anguilla. It consists of pellets of various sizes, some decidedly spherulitic, which have an aggregate refractive index of 1.62 to 1.64 and are very birefringent. All are peppered with minute grains having both very high refractive index and very high birefringence. The grains probably are titanium oxide. Hematite appears in small grains, some of which are spherulitic. Quartz grains are present but not abundant. X-ray examination shows abundant boehmite, little hematite and quartz, and kaolinite, probably. Stains color the pellets unevenly, but tests on artificial boehmite show that it is porous enough to stain decidedly.

TABLE II.

Location and Depth of *Carnegie* Bottom Samples.

Sample No.	Lat.	Long.	Depth meters	Approximate location
21	33 59 S.	106 43 W.	3139	2000 miles W. of Valparaiso
27	31 54 S.	88 17 W.	3879	1000 miles W. of Valparaiso
29	24 57 S.	82 15 W.	1089	700 miles W. of Northern Chile
57	37 40 N.	145 26 E.	5396	200 miles off the coast of Japan
61	44 16 N.	137 37 W.	4081	600 miles W. of Oregon
62	40 37 N.	132 23 W.	3785	400 miles W. of Oregon
64	33 49 N.	126 20 W.	4418	400 miles W. of Los Angeles
65	31 38 N.	128 48 W.	4251	1000 miles W. of Los Angeles
77	21 18 N.	138 36 W.	5320	Mid-ocean between Hawaii and Lower California
79	12 40 N.	137 32 W.	4918	Mid-ocean between Hawaii and Panama
80	7 45 N.	141 24 W.	5003	Mid-Pacific west of Panama
85	10 54 S.	161 53 W.	2614	East of Samoa

STUDIES OF SOLUBILITY IN SYSTEMS CONTAINING
ALKALI AND WATER: I. GENERAL INTRODUCTION.
II. A FILTER AUTOCLAVE FOR SOLUBILITY MEAS-
UREMENTS AT ELEVATED TEMPERATURES AND
ATMOSPHERIC PRESSURE. III. SOLUBILITY OF
NaOH IN A SATURATED Na_2CO_3 SOLUTION BETWEEN
60 AND 70° C.

GEORGE W. MOREY AND JOHN S. BURLEW.

ABSTRACT.

The application of physico-chemical principles to the problems of pegmatite formation and the hydrothermal alteration of minerals requires knowledge of the solubility or fusion surface of the system, $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, at temperatures below about 600° C. As a first step toward gaining this knowledge a new type of autoclave has been designed for solubility studies by the analytical method. With it a mixture of solid and liquid at a constant temperature can be stirred in a silver vessel and then filtered through a platinum felt, after which the filtrate is cooled and analyzed. Such an autoclave for use at atmospheric pressure has been perfected during investigation of part of the system, $\text{NaOH}-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$, at elevated temperatures. The liquidus temperatures along the boundary curves $\text{NaOH}.\text{H}_2\text{O}-\text{Na}_2\text{CO}_3$ and $\text{NaOH}-\text{Na}_2\text{CO}_3$ between 60 and 70° now are reported, together with the optical properties of $\text{NaOH}.\text{H}_2\text{O}$ and NaOH .

I. GENERAL INTRODUCTION.

Various problems concerning the natural occurrence of minerals have been solved by the application of physical chemistry. Of the many minerals whose origins are still little understood, analcite ($\text{H}_2\text{NaAlSi}_2\text{O}_7$), muscovite ($\text{H}_2\text{KAl}_3\text{Si}_3\text{O}_{12}$), and natrolite ($\text{H}_4\text{Na}_2\text{Al}_2\text{Si}_8\text{O}_{12}$) are examples that are quaternary compounds in the system, $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Orthoclase (KAlSi_3O_8), nephelite (NaAlSiO_4), and pyrophyllite ($\text{H}_2\text{Al}_2\text{Si}_4\text{O}_{12}$) are ternary compounds in the same system. In the endeavor both to explain the paragenesis of the former group and to predict the action of hot aqueous solutions on the latter group, it is necessary to begin by the formulation of the phase relations in this five-component system—which relations sometimes are complicated by interaction with carbon dioxide. Only by such a systematic procedure can we equal the success attained by van't Hoff and his coworkers¹ in unraveling the

¹ van't Hoff, J. H., *et al.*: Untersuchungen über die Bildungsverhältnisse der Ozeanischen Salzablagerungen insbesondere des Stassfurter Salzlagers; Akademische Verl., Leipzig, 1912.

mysteries of the Stassfurt salt deposits or that attained more recently by Bowen² in predicting the composition of residual liquids of crystallizing magmas as exemplified by rhyolites, trachytes, and phonolites. To follow an opposite course by undertaking more hydrothermal syntheses of minerals would produce no results beyond additions to a sixty-year-old accumulation of information that cannot of itself be systematized. Once the phase relations are known, however, they should provide the explanation of the results³ of individual hydrothermal syntheses.

After the completion of the first quantitative investigation of phase equilibria in the system, alkali—alumina—silica—water (the study⁴ of the system, $\text{H}_2\text{O}—\text{K}_2\text{SiO}_3—\text{SiO}_2$, in this Laboratory twenty years ago), it was realized that before the work could be extended, it would be necessary to examine the two limiting ternary systems that do not contain water. Thanks to the work done since then by several investigators,⁵ mostly in this Laboratory, the phase relations in the systems, $\text{Na}_2\text{O}—\text{Al}_2\text{O}_3—\text{SiO}_2$ and $\text{K}_2\text{O}—\text{Al}_2\text{O}_3—\text{SiO}_2$, are understood, except near the two binary borders $\text{Na}_2\text{O}—\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}—\text{Al}_2\text{O}_3$. With the aid of this knowledge, it has been possible to resume

²Bowen, N. L.: This Journal, 33, 1-21, 1937.

³For an annotated bibliography of hydrothermal syntheses, see Morey, G. W., and Ingerson, Earl: *Econ. Geol.*, 32, 607-761, 1937.

⁴Morey, G. W., and Fenner, C. N.: *J. Am. Chem. Soc.*, 39, 1173-1229, 1917.

⁵ SiO_2 . Fenner, C. N.: This Journal, 36, 331-384, 1913; Wietzel, R.: *Z. anorg. allgem. Chem.*, 116, 71-98, 1921; Greig, J. W.: This Journal, 13, 1-44, 1927.

$\text{Al}_2\text{O}_3—\text{SiO}_2$. Bowen, N. L., and Greig, J. W.: *J. Am. Ceram. Soc.*, 7, 238-254, 1924; Bowen, N. L., Greig, J. W., and Zies, E. G.: *J. Wash. Acad. Sci.*, 14, 183-191, 1924.

$\text{Na}_2\text{O}—\text{SiO}_2$. Morey, G. W., and Bowen, N. L.: *J. Phys. Chem.*, 28, 1167-1179, 1924; D'Ans, J., and Löffler, J.: *Z. anorg. allgem. Chem.*, 191, 1-35, 1930; Kracek, F. C.: *J. Am. Chem. Soc.*, 52, 1436-1442, 1930; Kracek, F. C.: *J. Phys. Chem.*, 34, 1583-1598, 1930.

$\text{K}_2\text{SiO}_3—\text{SiO}_2$. Kracek, F. C., Bowen, N. L., and Morey, G. W.: *J. Phys. Chem.*, 33, 1857-1879, 1929; Goranson, Roy W., and Kracek, F. C.: *J. Phys. Chem.*, 36, 913-926, 1932; Kracek, F. C., Bowen, N. L., and Morey, G. W.: *J. Phys. Chem.*, 41, 1183-1193, 1937.

$\text{Na}_2\text{SiO}_3—\text{K}_2\text{SiO}_3—\text{SiO}_2$. Kracek, F. C.: *J. Phys. Chem.*, 36, 2529-2542, 1932.

$\text{Na}_2\text{SiO}_3—\text{Na}_2\text{Si}_2\text{O}_7—\text{NaAlSi}_3\text{O}_8$. Tilley, C. E.: *Mineralog. petrog. Mitteilungen (Z. Krist., Abt. B)* 43, 406-421, 1933.

$\text{NaAlSi}_3\text{O}_8—\text{KAlSi}_3\text{O}_8$. Bowen, N. L.: This Journal, 43, 115-132, 1917; Bowen, N. L., and Greig, J. W.: This Journal, 10, 204-212, 1925.

$\text{NaAlSi}_3\text{O}_8—\text{KAlSi}_3\text{O}_8—\text{SiO}_2$. Rice, B. A.: *J. Am. Ceram. Soc.*, 6, 525-547, 1923; Schairer, J. F., and Bowen, N. L.: *Trans. Am. Geophys. Union*, 16, 325-328, 1935.

KAlSi_3O_8 . Morey, G. W., and Bowen, N. L.: This Journal, 4, 1-21, 1922.

the inquiry into the two quaternary systems, $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, with attention limited at present, for the sake of simplicity, to constituent binary and ternary systems.

METHODS OF STUDY OF PHASE EQUILIBRIA.

A problem as broad as this one must be attacked piecemeal by a variety of methods. In working out the phase relations in the anhydrous systems just mentioned, the two standard procedures were quenching⁶ and thermal analysis.⁷ The former was employed in the determination of liquidus temperatures and the latter in the determination of phase changes in the solid state. The modification⁸ of thermal analysis for use with substances having a high vapor pressure probably can be used when necessary in studying solid phases in the systems involving water. The quenching method already has been modified in several respects for use in those regions of the system, alkali—alumina—silica—water, in which crystallization is sluggish, so that a small sample just above the liquidus temperature can be quenched to a glass. In the study of the system, $\text{H}_2\text{O}-\text{K}_2\text{SiO}_3-\text{SiO}_2$, most of the measurements were performed by the "hydrothermal quenching method."⁹ in which the quenching took place in a bomb in the presence of the water vapor that had been in equilibrium with the melt. A number of other samples were quenched in an ordinary quenching furnace through which steam was passed at atmospheric pressure. By means of the former procedure the isothermal polybaric saturation curves were obtained in the temperature range 200 to 600°, and by means of the latter the isobaric polythermal saturation curve at one atmosphere was obtained. Recently a considerable advance has been made by the development of apparatus¹⁰ for the simultaneous extension of the method of quench-

⁶ Introduced by Shepherd. [Shepherd, E. S., Rankin, G. A., and Wright, F. E.: *This Journal*, 28, 293-333, 1909; p. 308.]

⁷ For a description of its application to a silicate, see Kracek, F. C., Bowen, N. L., and Morey, G. W.: *J. Phys. Chem.*, 33, 1857-1879, 1929 (pp. 1874-1878); 41, 1183-1193, 1937 (pp. 1187-1191).

⁸ Kracek, F. C.: *J. Phys. Chem.*, 34, 225-247, 1930 (p. 228).

⁹ Reference 4, pp. 1181-8. The success of the hydrothermal quenching method in this system was made possible by the low temperatures and pressures prevailing at saturation and by the ease of quenching a liquid to a glass from these low temperatures. There may be no other system in which the same favorable characteristics would be combined over such a wide range of compositions.

¹⁰ Morey, G. W., and Ingerson, Earl: *This Journal*, 35A, 217-225, 1938.

ing in steam to higher temperatures and high pressures. This new technique, it is hoped, will make possible the exploration of the saturation curves in that part of the system, alkali—alumina—silica—water, containing little water.

A related research that is being conducted by Goranson¹¹ concerns the effect of large hydrostatic pressure on the fusion temperature of silicate—water systems. Still another type of information is being sought in a study¹² of the distribution of water and carbon dioxide between the liquid and vapor phases in the system, $K_2O-SiO_2-H_2O-CO_2$, at temperatures above the liquidus.

None of these methods is conveniently applicable to regions in which compounds crystallize readily at relatively low temperatures (below say 500°). Furthermore, the synthetic method of solubility determination in a sealed tube, which was used successfully up to about 500° in the system boric oxide—water,¹³ will not yield accurate measurements in systems containing alkali, because of corrosion of the glass tube.

The behavior of saturated aqueous solutions at temperatures below about $600^\circ C.$ is especially interesting because of its bearing on several problems of petrography. The formation of pegmatites is ascribed¹⁴ generally to crystallization at a late stage during the cooling of an intrusive magma, by which time the percentage of water in the magma had increased considerably because of the crystallization of anhydrous phases. The aqueous solutions remaining from the crystallization of pegmatites, containing a still higher percentage of water at a still lower temperature, occasioned hydrothermal alteration of previously solidified minerals and finally left deposits of secondary minerals in veins. The temperature at the beginning of the pegmatitic stage is a matter of speculation; but it seems likely that the temperature at the end was not far from $500^\circ C.$ Thus that portion of the fusion surface of the system, alkali—alumina—silica—water, that lies at temperatures below 600° is concerned directly in any attempt to explain the order of crys-

¹¹ Goranson, R. W.: *Trans. Am. Geophys. Union*, 17, 257-9, 1936; *This Journal*, 35A, 71-91, 1938.

¹² By G. W. Morey and M. Fleischer, cited in the *Annual Report of the Acting Director of the Geophysical Laboratory, Carnegie Institution of Washington Yearbook No. 36*, p. 115, 1937.

¹³ Kracek, F. C., Morey, G. W., and Merwin, H. E.: *This Journal*, 35A, 143-171, 1938.

¹⁴ For a comprehensive but not critical review of the opinions on the genesis of pegmatites, see Albert Johannsen: *A descriptive petrography of the igneous rocks*; Univ. of Chicago, Chicago, 1932; Vol. 2, pp. 77-84.

tallization at the end of the pegmatitic stage and during the entire course of the periods of hydrothermal alteration and of deposition in veins. In connection with these latter processes it is important to emphasize that a high degree of solubility of a solid phase in the aqueous solution was not required for considerable reaction to have taken place: all that was required was that the products of the reaction should have been removed in some manner,—as by deposition elsewhere,—the presence of the material in the solution having been merely an intermediate step.

ANALYTICAL METHOD OF SOLUBILITY DETERMINATION.

In the effort to find a suitable method for the study of such solutions in the system, alkali—alumina—silica—water, the readiness to crystallize that makes difficult the use of the quenching method was turned to account by trying the analytical method of solubility determination, in which ease of crystallization is a prerequisite to success. Although a complete bibliography of the various applications of the analytical method would be very long, it would include few attempts to apply this method to alkaline solutions at high temperatures.

Koenigsberger and Müller¹⁵ constructed an apparatus that in principle would have served for solubility determinations by the analytical method, although the only use they made of it was for the separation of the solid phase in hydrothermal syntheses of alkaline silicate minerals. This apparatus was similar in some respects to that which had been used by Tilden and Shenstone¹⁶ in the determination of the solubility of a number of salts in water between 100 and 200° C. The reaction vessel was a cylindrical steel bomb (inside dimensions: 25 x 400 mm.) lined with platinrhodium. It fitted inside an insulated electric furnace that was mounted in a framework in such a way that it could be shaken three times a second by an eccentric driven by an electric motor. A device for filtration inside the reaction chamber consisted of two platinrhodium tubes, each half as long as the reaction chamber but of different diameters. The larger, which was the filter tube proper, fitted snugly inside the

¹⁵ Koenigsberger, J., and Müller, W. J.: *Centr. Mineral. Geol.*, 1906, 339-348; 353-372; Müller, W. J., and Koenigsberger, J.: *Z. anorg. allgem. Chem.*, 104, 1-26, 1918; Koenigsberger, J.: *Fortschr. Mineral. Krist. Petrog.*, 11, 41-48, 1927.

¹⁶ Tilden, W. A., and Shenstone, W. A.: *Trans. Roy. Soc. (London)*, 175, 23-36, 1884.

reaction chamber. One end, which was at the top of the chamber when the apparatus was in the normal position, was open; and the other end was covered with a fine platinum sieve. One end of the smaller tube (5 mm. diameter) was fastened through the center of the sieve; and the other end, which extended almost to the bottom of the chamber, was covered also with a platinum sieve. After the reaction mixture had been agitated for the desired length of time, the furnace (and therefore the reaction tube also) was turned upside down. The reaction mixture then rested on the sieve covering the filter tube. As the liquid phase dripped slowly through the sieve, the smaller tube permitted gas to displace it in the upper half of the chamber. After filtration had been completed in six to 24 hours, the furnace was cooled slowly to room temperature, the bomb was opened, and the two phases were separated. The three chief objections to this design (if the apparatus were to be used for solubility determinations) are: (a) the agitation of the reaction mixture is inadequate; (b) temperature uniformity is difficult to maintain (a difference of 3° between the two ends of the bomb was found by Koenigsberger and Müller); and (c) the time of filtration is much too long.

Waldeck, Lynn, and Hill¹⁷ used a bomb constructed of 18-8 stainless steel in the determination of the solubility of Na_2CO_3 in water up to 348° and of isotherms in the system, $\text{Na}_2\text{CO}_3\text{—NaHCO}_3\text{—H}_2\text{O}$, up to 200° . The bomb (capacity, 135 cc.) was oscillated in an air thermostat until equilibrium was reached. A sampling tube, set into the head of the bomb (in the later model) and operated externally by a needle valve, permitted removal of part of the liquid phase after the solid phase had settled. Bombs of this same design were used by Schroeder and his coworkers¹⁸ in measurements of the solubility equilibria of sodium sulphate in solutions of sodium hydroxide and other sodium compounds up to 350°C . They added a blow-off valve at the bottom, in order to secure a sample of dry solid phase. The chief objections to this design are: (a) the agitation of the reaction mixture is inadequate; (b) contamination by corrosion is present; (c) the solid phase of a slightly viscous mixture or of one containing very fine crystalline particles (a

¹⁷ Waldeck, W. F., Lynn, George, and Hill, A. E.: *J. Am. Chem. Soc.*, 54, 928-936, 1932; 56, 43-47, 1934.

¹⁸ Schroeder, W. C., Gabriel, Alton, and Partridge, E. P.: *J. Am. Chem. Soc.*, 57, 1539-1546, 1935; Schroeder, W. C., Berk, A. A., and Gabriel, Alton: *J. Am. Chem. Soc.*, 58, 843-849, 1936; 59, 1783-1790, 1937.

desirable condition in itself) would not be removed completely from the liquid phase because of the lack of a filter; (d) removal of the filtrate from the sampler would be difficult, if it solidified in it, as would some filtrates obtained at high temperatures; and (e) precise temperature control of such a large apparatus in an air thermostat is difficult.

The reaction vessel used by Seyer and Todd¹⁹ in the determination of the solubility of Na_2CO_3 up to 173° consisted of an iron tube with a side-arm. After the mixture had been agitated by rotation of the tube and then allowed to settle, some of the solution was decanted into the side-arm. Vasil'ev²⁰ in the determination of the solubility of Na_2CO_3 and of K_2CO_3 up to 200° used a glass tube of somewhat similar design. Neither arrangement would furnish accurate results with alkali-water systems at high temperatures, because of contamination by the products of corrosion, the lack of active agitation, and the lack of complete filtration.

Hitchen²¹ devised an apparatus to study hydrothermal solubility and used it to measure the solubility of silica in water from 128 to 336° . A large reaction chamber (volume, 1365 cc.) made of 18-8 stainless steel was supported in an electrically-heated air thermostat. To the head of this pressure vessel was attached a re-entrant thermocouple well and a connection to a pressure gauge. The large size of reaction chamber had been chosen so that a number of 100-cc. samples could be taken for analysis without renewing the charge. Each was withdrawn from the bottom of the chamber through a needle valve that was connected to a weighed steel sampling tube surrounded by a water jacket. The hole leading from the bottom of the reaction chamber into the needle valve was covered with a filter cup that contained graded layers of particles of some inert material—silica in the experiments on the solubility of silica. Although this design was satisfactory for researches with solutions of silica, its use for alkaline solutions, for which its originator had hoped to employ it later, is attended by several objections: (a) lack of agitation of the reaction mixture (equilibrium in a silica solution at 300° was reported to have been reached in ten hours without agitation); (b) contamina-

¹⁹ Seyer, W. F., and Todd, Eric: *Trans. Roy. Soc. Can.*, 23-III, 67-70, 1929.

²⁰ Vasil'ev, B. B.: *Trans. State Inst. Applied Chem. (U. S. S. R.)*, No. 23, 110-117, 1935.

²¹ Hitchen, C. S.: *Bull. Inst. Mining Met.*, Nos. 364, 366, and 375, 1935. Printed also in *Trans. Inst. Mining Met.*, 44th session, 1934-1935, pp. 255-336.

tion by corrosion (only very slight with the silica solutions); (c) crystallization of filtrate in the needle valve during filtration; and (d) change of composition of the solution by the evaporation that would accompany the decrease of pressure during sampling.

Successful application of the analytical method of solubility determination requires:

- (1) A containing vessel that does not contaminate the solution by products of its corrosion.
- (2) Active agitation of the solution to facilitate the attainment of equilibrium.
- (3) Precise control and measurement of the temperature of the solution during agitation.
- (4) A means of filtration that removes every trace of solid phase without disturbing the equilibrium either by a temperature change or by altering the liquid-vapor equilibrium.
- (5) A means of bringing the filtrate to atmospheric pressure and temperature without changing its composition.
- (6) Accurate analysis of the filtrate.
- (7) Identification of the solid phase or phases that had been present in equilibrium with the solution.

With non-corrosive reaction mixtures near room temperature, these conditions are fulfilled easily. In the several forms of apparatus that have just been reviewed, one or more of these requirements had not been met, as already has been pointed out. For the investigation of solubility equilibria in alkaline solutions at elevated temperatures, all of them have been satisfied by the filter autoclave and technique that will be described in Part II of the present paper.

APPLICATION OF THE FILTER AUTOCLAVE.

During the development of the filter autoclave as a precision instrument, we chose to work with the system, $\text{NaOH}-\text{H}_2\text{O}$, because the vapor pressures of solutions saturated with respect to NaOH are less than atmospheric pressure; and therefore the basic principles of the autoclave could be perfected without the complication of high pressures. The ease of analysis of filtrates in this system also influenced our choice. Inasmuch as it is impossible without working in a vacuum to obtain and keep NaOH free of carbonate, it was decided to find out how much effect CO_2 has on the solubility of NaOH at high temperatures. The information gained concerning the system, $\text{NaOH}-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$, which in itself is of general chemical interest.

will be helpful in the subsequent study of alkali—water systems of greater complexity.

Since the autoclave has been perfected, it has been used to determine the boundary between the NaOH and Na_2CO_3 fields in the system, $\text{NaOH}—\text{Na}_2\text{CO}_3—\text{H}_2\text{O}$. So soon as the determination of the isotherms in the field of NaOH up to 300° has been completed, these results will be published. The determination of the solubility of $\text{NaOH} \cdot \text{H}_2\text{O}$ in a saturated Na_2CO_3 solution, which is described in Part III of the present paper, is an especially severe test of the method, for although a change of two per cent in the composition of the solution alters the liquidus temperature only one degree, it was possible to obtain a smooth liquidus curve that shows the rise of only two and one-half degrees from the eutectic temperature to the maximum temperature along the curve of double saturation.

An earlier form of this autoclave had been used by Morey²² to determine the 125° isotherm in the system, $\text{Na}_2\text{O}—\text{SiO}_2—\text{H}_2\text{O}$. We have performed experiments in this system at higher temperatures; but they were unsuccessful, because the vapor pressure of the solution was sufficiently above atmospheric pressure for a considerable quantity of water vapor to leak out past the stirrer shaft, thereby progressively changing the composition of the solution. For the study of such systems a high-pressure-steam filter autoclave is now under construction. It will be a pressure vessel with an oil-sealed stuffing box for the stirrer shaft, and it will be connected to a steam boiler kept at a constant temperature in a separate furnace, whereby steam at a constant pressure will be supplied during stirring and filtration. With this new apparatus it is hoped that solubility determinations can be carried out at temperatures up to 500°C . and at pressures up to 200 bars in large regions of the systems, $\text{NaOH}—\text{Na}_2\text{CO}_3—\text{H}_2\text{O}$, $\text{Na}_2\text{O}—\text{SiO}_2—\text{H}_2\text{O}$, $\text{Na}_2\text{O}—\text{Al}_2\text{O}_3—\text{H}_2\text{O}$, and the corresponding potassium systems.

II. A FILTER AUTOCLAVE FOR SOLUBILITY MEASUREMENTS AT ELEVATED TEMPERATURES AND ATMOSPHERIC PRESSURE.

The filter autoclave that was designed to meet the requirements for solubility measurements in alkaline solutions at elevated temperatures, as set forth in Part I of this paper, is shown

²² Morey, G. W., quoted in Vail, James G.: Soluble silicates in industry; Chem. Catalog Co., New York, 1928, pp. 116-7.

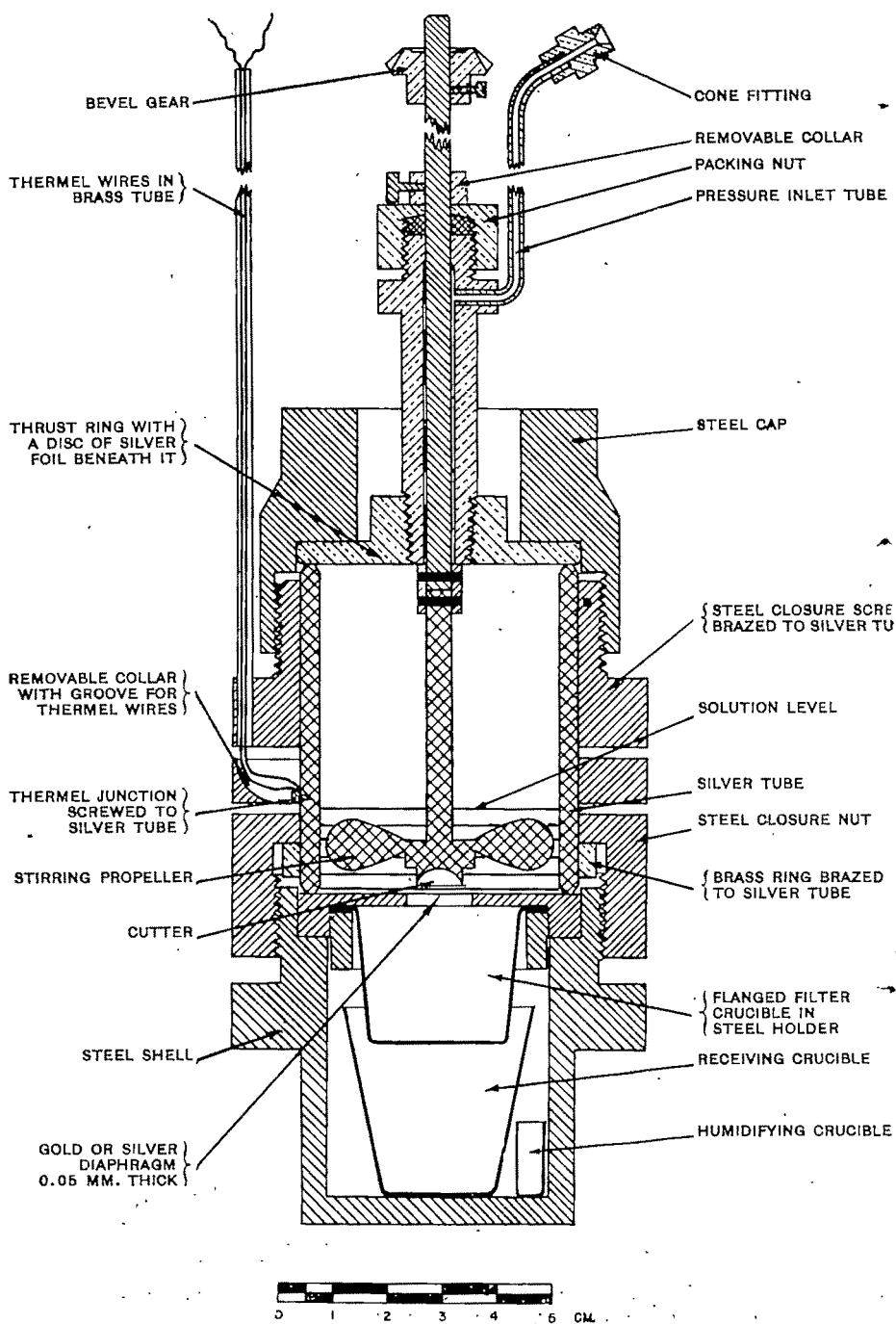


Fig. 1. Filter Autoclave.

in cross-section in Fig. 1. It consists of three principal units: a lower chamber that contains a platinum crucible (capacity, 25 cc.) to receive the filtrate, a reaction chamber in which the mixture of solid and liquid is stirred by a propeller, and a combination stirrer-shaft-bearing and gas inlet tube that is fastened to the top of the reaction chamber by means of a steel cap.

A steel disc with a 13-mm. hole in its center rests on a shoulder inside the top of the steel shell that forms the lower chamber. To its under side is attached a flanged platinum filter crucible²³ by means of a lens ring that is screwed into a recess in the disc. The joint is made tight by a silver gasket (0.10 mm. thick) beneath the flange. The perforated bottom of the filter crucible is covered with a highly burnished platinum felt. A silver tube forms the walls of the reaction chamber. A steel closure nut that encircles this tube screws on the top of the lower steel shell. Thus, when the autoclave is assembled, the diaphragm (0.05 mm. thick) that forms the bottom of the reaction chamber is held tightly between the face of the steel disc and the beveled end of the silver tube. Before assembly of the autoclave at the beginning of an experiment, the end of the silver tube and the face of the steel holder are polished with very fine emery on a lapping plate. Tests with prussian blue at various times have shown that after these parts have been polished, the line of contact between them is continuous.

After some experiments at 180° and higher temperatures, it was found that the silver diaphragm had become welded to the end of the silver tube, and had to be cut away. Gold diaphragms of the same thickness were tried; but welding still took place. Because of their color, the pieces of gold that adhered to the silver tube could be seen easily, and therefore could be cut away without damage to the tube. Hence gold diaphragms have been used in many of the experiments at temperatures above 180°.

The stirrer shaft is stainless steel except for the part inside the reaction chamber, which is pure silver. To its lower end is screwed a pure silver propeller, and below that a cutter with which to cut a hole in the silver diaphragm to let the mixture pass from the reaction chamber into the filter crucible. The cutter, which operates like a cork-borer, was made from an

²³ A "Munroe crucible." For its history and for incomplete directions for the formation of the platinum felt, see W. O. Snelling: *J. Am. Chem. Soc.*, 31, 456-61, 1909.

alloy²⁴ containing 90 per cent Ag and 10 per cent Ni that was cast especially for this purpose. Its sharpened end has a circular cross-section with a diameter of 9 mm. Above the reaction chamber the stirrer shaft passes through a bearing tube on top of which is a stuffing box and packing nut. The packing is an asbestos cord impregnated with graphite. The lower end of the bearing tube is fastened into a thrust ring that is held against the top of the silver tube by a screw cap. The joint is made tight by a silver gasket (0.20 mm. thick) beneath the thrust ring. The stirrer shaft is kept in position by a shoulder that bears against the under side of the thrust ring at the same time that a removable collar bears against the top of the packing nut. Just below the stuffing box a small copper tube has been brazed to the bearing tube. It is bent upward parallel to the stirrer shaft, and has a cone fitting on its upper end in order that a connection can be made to a tank of compressed nitrogen.

Furnace. The autoclave is heated in an air bath, formed by a hollow brass cylinder with a thick brass bottom (outside diameter, 12.2 cm.; inside diameter, 8.8 cm.; inside depth, 16.6 cm.; outside length, 19.7 cm.; weight, with cover, 11.3 kg.). This brass cylinder fits snugly inside a refractory furnace tube (wall thickness, 1.5 cm.; length, 37 cm.), on the outside of which has been wound a heater of nichrome wire. The furnace tube sits within a sheet-metal shell (diameter, 25.6 cm.; height, 37.5 cm.), the annular space being filled with powdered magnesia. A wooden box (top, 39 x 39 cm.; height, 43 cm.) surrounds the furnace. A brass cover fits over the air bath just above the steel cap of the autoclave; and the furnace tube and wooden box have separate covers, the center sections of which are removable. The furnace is bolted to a steel casting (diameter, 44 cm.; thickness, 2.3 cm.), to which is attached also a steel bar that serves as a pillar on the top of which a motor is pivoted at such a height that a bevel gear on its shaft can engage another on the upper end of the stirring shaft of

²⁴ This alloy apparently has not been described previously. According to the phase equilibrium diagram of Petrenko [Petrenko, G. J.: *Z. anorg. allgem. Chem.*, 53, 212-5, 1907, reproduced (with some temperatures corrected) in *Int. Crit. Tables*, Vol. 2, p. 422, and in Hansen, M.: *Der Aufbau der Zweistofflegierungen*, Berlin, 1936, p. 43] this alloy consists of a matrix of pure silver in which is dispersed a few per cent of a solid solution containing 96 per cent Ni and 4 per cent Ag. We intend to study further the alloy system silver-nickel.

the autoclave. The speed of stirring is thirty revolutions a minute.

The furnace heater is connected to a 115-volt line through a "Variac."²⁵ Because the voltage of the current is kept constant by the main laboratory voltage regulator and because the furnace is so well insulated, it has been possible to dispense with an automatic temperature controller. A particular setting of the Variac will cause attainment of the same temperature within a degree or two on different occasions. Infrequent manual variation of the power input keeps the temperature of the autoclave constant within 0.1°C .

Thermocouples. The temperature of the autoclave is measured with a platinum vs. platinum (90)—rhodium (10) thermocouple junction that is held by a screw tightly against the outside of the silver tube about one centimeter from the bottom. A removable collar that is fastened around the tube protects the junction from convection currents and from radiation from the furnace wall. The wires leading from the junction, insulated by two concentric porcelain tubes, pass up through a 4-mm. brass tube that fits in a hole through the rim of the top steel closure screw of the autoclave. The temperature of the brass cylinder that forms the air bath is measured separately with a glass-enclosed platinum vs. platinum-rhodium junction in a well ten centimeters deep.

These two thermocouple junctions are connected to a cold junction that has a common platinum-rhodium wire. The cold junction, which is imbedded in paraffin in a glass tube, is kept in melting ice and distilled water in a vacuum-jacketed bottle. The connections between the leads from the hot junctions and the corresponding ones from the cold junction, which are held together by spring clips, are protected from draughts by a small wooden box.

The emf. of each thermocouple is measured with a modified Wolff-type potentiometer (No. 3530), used in conjunction with a Weston galvanometer (Model 99, No. 3) and an Eppley unsaturated standard cell that is packed in glass wool in a wooden box.

The galvanometer sensibility has been adjusted to $0.5\text{ }\mu\text{v}$ per scale division. Deflections, which are kept less than $6\text{ }\mu\text{v}$, are estimated to the nearest $0.1\text{ }\mu\text{v}$. The small corrections found in a calibration of the potentiometer coils in May, 1936 are

²⁵ A variable transformer (type 200), made by the General Radio Co.; Cambridge, Mass.

applied to all readings. Under these conditions an emf. can be measured to $\pm 0.5 \mu\text{v}$.

The potentiometric system is doubly shielded as recommended by White,²⁶ with the inner shield connected to the case terminal of the galvanometer. There is also an internal battery shield. Inasmuch as the autoclave is connected electrically to the thermocouple, it has been necessary to insulate the motor shaft from the autoclave by a hard rubber bushing. With these precautions the galvanometer circuit shows no deflection when either the motor circuit or the heating circuit is broken. The small internal parasitic emf. (less than $1 \mu\text{v}$) is circumvented by a combination selector-eliminating switch with an all-copper circuit, designed by W. P. White.

The thermocouple in the shell of the air bath has not been calibrated. The thermocouple connected to the autoclave (Th. 372/370B) and another new thermocouple (Th. 374/370A) were calibrated simultaneously in April, 1937 at the ice, steam, tin, and lead points with a maximum uncertainty of $\pm 1 \mu\text{v}$. At the same time the difference in emf. between them at these different fixed points was measured directly. After this calibration Th. 374/370A was preserved as a reference standard. It was recalibrated in January, 1938 at the same fixed points. The greatest difference between the two sets of results was $0.6 \mu\text{v}$.

The results of all calibrations are expressed in the form of deviations from the "standard emf. values" listed in Adams' table,²⁷ which is used in this research to convert the emf. of a thermocouple to a temperature on the scale of the Geophysical Laboratory. This scale differs from the International Temperature Scale²⁸ by not more than 0.4° at temperatures below 600° .

Immediately after the calibration of Th. 372/370B and Th. 374/370A, they were compared with each other while the hot junction of the former was screwed to the outside of the autoclave tube in its normal position and the hot junction of the latter, enclosed in a very thin glass tube, rested on the diaphragm inside the autoclave. In lieu of a reaction mixture, sodium chloride was placed around this junction to a depth of fifteen millimeters. The autoclave was heated in the air bath to a constant temperature, and the difference in emf. between the two thermocouples was measured five times at intervals of

²⁶ White, W. P.: *J. Am. Chem. Soc.*, 36, 2011-2020, 1914.

²⁷ Adams, L. H.: *J. Am. Chem. Soc.*, 36, 65-72, 1914; *Int. Crit. Tables*, Vol. 1, p. 57, 1926.

²⁸ Burgess, G. K.: *Bur. Standards J. Research*, 1, 635-640, 1928.

ten minutes. The maximum difference observed at any of four temperatures between 100 and 327° was 0.5 μv , which is equivalent to a difference of only 0.05° between the temperature measured in the usual way and that indicated inside the autoclave.

A series of four similar experiments was performed, with the hot junction of Th. 374/370A passing through a hole in the diaphragm and resting on the bottom of the filter crucible. Under these conditions the temperature measured in the usual way was a little lower than that measured with the thermocouple in the filter crucible. The difference was almost directly proportional to the temperature of the autoclave, reaching 0.6° at 280°.

Even this maximum difference in temperature between the reaction mixture and the filter crucible cannot affect the accuracy of the measurements. A calculation based on the heat capacities of the crucible and of ten grams of filtrate shows that if the total excess heat of the crucible corresponding to a temperature difference of 0.6° were absorbed by the filtrate, the temperature of the latter would be increased less than 0.1°. This increase can do no harm; on the contrary, it furnishes assurance that no precipitation occurs during filtration.

After Th. 372/370B had been in use several months, it was recalibrated against Th. 374/370A, with the latter resting on the diaphragm on the inside of the autoclave just as during the initial comparison. When Th. 372/370B had been new, its emf. was slightly greater than the standard value for a given temperature (1.5 μv at 2000 μv); but at the time of the second calibration its emf. was lower (3.3 μv at 2000 μv). At four subsequent calibrations during the next nine months, the fluctuations of the deviation curve amounted to less than ± 2 μv throughout the range 400 to 2600 μv .

The change from one period of calibration to the next is so slight that the total uncertainty introduced in a temperature measurement by the uncertainty of the calibration is not more than $\pm 0.1^\circ$. Hence, the maximum relative uncertainty of the equilibrium temperature during a solubility determination with the filter autoclave is $\pm 0.2^\circ$, when the maximum observed variation of temperature during the period of equilibrium is $\pm 0.1^\circ$ (as is usually the case). The maximum uncertainty of any temperature with respect to the thermodynamic temperature scale, however, is $\pm 0.5^\circ$, because of the uncertainty of interpolation²⁹ between fixed points.

²⁹ Roeser, W. F., and Wensel, H. T.: *J. Research Nat. Bur. Standards*, 14, 247-282, 1935; Table 9, p. 280.

Corrosion. During the development of the autoclave, the first cutter of the present type that was tried was made of Monel metal. In an $\text{NaOH—Na}_2\text{CO}_3$ solution at 180° it corroded badly, producing a pale green color in the filtrate, because of the presence of ferrous iron. When the filtrate was dissolved in water, the iron became oxidized to $\text{Fe}(\text{OH})_3$, which was precipitated. Metallic copper in the mixture inhibited the attack on the iron in the Monel metal; but finely divided copper was precipitated on the cutter and also appeared in the filtrate. When the filtrate was dissolved, the copper reacted to form blue cupric ions. The corrosion seemed not to affect the Na_2O content of the filtrate very much; but it did increase by one part in thirty the amount of CO_2 present at double saturation at 180° . Also the values obtained for the CO_2 content when corrosion was present were more irregular than those obtained in the absence of corrosion.

Even with a reaction chamber that is completely silver-lined (except for the silver-nickel alloy of the cutter) some corrosion of the metal occurs, as evidenced by the whitening of the silver at temperatures above 100° . In some of the experiments at high temperatures in which a gold diaphragm was used, it became covered with a layer of silver thick enough to cause a perceptible whitening of the surface.

Technique. The use of the filter autoclave may be described in terms of the standard procedure that is being used in the determination of solubilities in the system, $\text{NaOH—Na}_2\text{CO}_3\text{—H}_2\text{O}$. In a typical experiment a charge of total weight between 35 and 40 grams was made up from NaOH pellets, $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$, and H_2O in proportions to give between 5 and 10 grams of solid phase at equilibrium. The charge was sealed in the autoclave late one afternoon, with a cap on the pressure inlet tube, and the autoclave was placed in the preheated furnace overnight.

Early the next morning the stirrer was started by means of a time switch. A measurement four hours later showed that the temperature was a few degrees above the desired equilibrium value (in a companion experiment the "Variac" was set to give a temperature a few degrees below the equilibrium value). The furnace was cooled rapidly for a short time, and then more slowly as the autoclave approached the equilibrium temperature, which was reached in about two hours. Stirring had been continued during the period of cooling; and it was continued four hours longer, during which time the tempera-

ture remained within 0.1° of the equilibrium value as shown by observations made every ten minutes.

At the end of the period of constant temperature, stirring was stopped; the cap was removed from the pressure inlet tube; and a hole was cut in the diaphragm by loosening the collar on top of the packing nut and pushing down on the stirring shaft while rotating it slowly. The melt was allowed to drain through the hole for two minutes. A pressure of 20 lb. of nitrogen was applied through the pressure inlet tube in the course of one-half minute and then was maintained for five minutes, to force the solution through the filter.

Evaporation during filtration was prevented by having the same pressure of water vapor in the lower chamber as had existed in the reaction chamber at equilibrium. This was accomplished by having in the lower chamber a small crucible (the "humidifying crucible" in Fig. 1), in which at the start of the experiment had been placed a one-gram charge that contained a few centigrams of water in excess of the approximate composition of the liquidus. When the autoclave had been heated, some of the water had evaporated and had filled the lower chamber, remaining in equilibrium with the saturated solution in the humidifying crucible, so that at the time of filtration the proper humidity was present there. This precaution probably was not important at temperatures below 200° ; but at higher temperatures it contributed to the accuracy of the measurements.

The nitrogen gas itself did not change the composition of the filtrate, because of the preliminary period of drainage, and because of the slowness with which the gas was admitted. Under these conditions the nitrogen became warmed in the upper chamber before it came in contact with the melt in the filter crucible.

After the nitrogen pressure had been applied for five minutes, it was released and the autoclave was removed from the furnace. It was cooled quickly first by having a fan blow air on it and then by placing it in running water. After the autoclave had been at room temperature for about 15 minutes, it was opened. The platinum crucible containing the filtrate, which had solidified on cooling, was removed from the lower chamber and placed quickly in a stoppered flask. The filtrate was weighed to ± 1 mg.

During the cooling no change in composition of the filtrate could occur, because the air that was drawn into the autoclave

had to pass through the filter crucible before it reached the filtrate: the pores of the filter retained enough NaOH to remove the small quantity of CO_2 and H_2O present in atmospheric air. After the autoclave was opened, however, an undetermined amount of CO_2 and H_2O was absorbed by the surface of the filtrate, by the time the crucible had been placed in the solution flask. The air of this flask also contained a little of these gases. Nevertheless, the total amount absorbed probably did not exceed a few milligrams. The observed weight of filtrate was not corrected to the time of removal of the filtrate from the autoclave, for the leading error was the actual weight of CO_2 absorbed (which subsequently was measured in the analysis) and not the proportional increase in weight of the filtrate.

After an experiment the autoclave was cleaned and the inside of the silver tube was polished. The platinum filter crucible was filled with 20 per cent HNO_3 . After the acid had dripped through, the filter was washed with distilled water by suction. Washing was continued until the filtrate gave no reaction with either phenolphthalein solution (absence of NaOH) or methyl orange (absence of HNO_3). The filter was dried in an oven at 125° for not less than three hours or at 400° for one-half hour. It was stored in a desiccator until the autoclave was assembled for the next experiment.

The solidified filtrate was dissolved in CO_2 -free distilled water the next morning; and the solution was analyzed in duplicate for Na_2O and CO_2 . The percentages of Na_2O and CO_2 found, together with the equilibrium temperatures, constituted the data obtained by this one experiment.

The total elapsed time required for a single experiment is about fifty hours, of which on the average the actual working time is fifteen hours, counting the time spent in keeping the apparatus in proper order, securing materials, and collating the data. By dovetailing several experiments, it is possible to complete three or four in a week.

III. SOLUBILITY OF NaOH IN A SATURATED Na_2CO_3 SOLUTION BETWEEN 60 AND 70°C .

PREVIOUS INVESTIGATIONS.

The solubility of sodium hydroxide monohydrate in water has been measured by Pickering⁸⁰ and by R. Dietz at the Reichs-

⁸⁰Pickering, S. U.: J. Chem. Soc., 63, 890-909, 1893.

anstalt.⁸¹ The former showed that $\text{NaOH}\cdot\text{H}_2\text{O}$ is the stable phase above 12°C ., that it melts congruently at 65° , and that it forms a eutectic with anhydrous NaOH at a temperature not much below its melting point. The latter's seven measurements (by the analytical method) in the range 0 to 64° gave a percentage of NaOH about one per cent less than that reported by Pickering at each of the same temperatures. Freeth,⁸² in his determination (by the analytical method) of the isotherms in the system, $\text{NaOH}\text{--}\text{Na}_2\text{CO}_3\text{--}\text{H}_2\text{O}$, at 0 , 15 , 30 , 45 , and 60° , did not carry his measurements all the way to the $\text{NaOH}\text{--}\text{H}_2\text{O}$ border, but made use there of the data of Pickering. His work demonstrated that Na_2CO_3 is the stable phase in alkaline solutions containing more than 35 per cent NaOH above 30°C ., and that at 60° the boundary between the $\text{NaOH}\cdot\text{H}_2\text{O}$ and Na_2CO_3 fields lies very close to the $\text{NaOH}\text{--}\text{H}_2\text{O}$ border.

In order to furnish a bridge between our contemplated measurements of the solubility of NaOH at elevated temperatures and the results of others at lower temperatures, we decided to extend our measurements to 60°C ., thus taking in a portion of the double saturation curve of $\text{NaOH}\cdot\text{H}_2\text{O}\text{--}\text{Na}_2\text{CO}_3$ on both sides of the maximum temperature. We were interested also to find out how the filter autoclave would behave near a congruent melting point and near a eutectic point.

EXPERIMENTAL PROCEDURE.

The solubility measurements were made with the filter autoclave, employing the technique outlined in Part II of the present paper.

Reagents. The starting material was C. P. NaOH in the form of pellets from the J. T. Baker Chemical Co. The label analysis on the bottle was as follows: Assay (NaOH), 98.7 per cent; Na_2CO_3 , 0.8 per cent; PO_4 , 0.0005 per cent; SO_4 , 0.002 per cent; Cl , 0.003 per cent; N , 0.0005 per cent; Fe , 0.001 per cent; heavy metals (as Ag), 0.001 per cent; SiO_2 and NH_4OH ppt., 0.00 per cent. Samples from this bottle were analyzed in duplicate for Na_2O and CO_2 , with these results: 98.36 per cent NaOH and 0.51 per cent Na_2CO_3 . The monohydrated sodium carbonate was of "reagent quality" from the Mallinckrodt Chemical Works. A fifty-gram sample of

⁸¹ Mylius, F., and Funk, R.: *Wiss. Abhandl. physik.-tech. Reichsanstalt*, 3, 449-458, 1900; p. 450.

⁸² Freeth, F. A.: *Trans. Roy. Soc. (London)*, 223 A, 35-87, 1923.

this same batch had been analyzed by E. G. Zies of this Laboratory, January, 1930, with the following results: SiO_2 , 0.0006 per cent; Cl as AgCl , 0.0008 per cent; SO_4 as BaSO_4 , nil; Fe_2O_3 and Al_2O_3 , 0.001 per cent; CaO , 0.001 per cent; MgO , nil; residue after neutralizing with HCl , 0.0003 per cent.

Preliminary Crystallization. When $\text{NaOH} \cdot \text{H}_2\text{O}$ was to be the solid phase, the charge was heated in the autoclave to 70° with stirring for an hour or two, and then cooled quickly to about 40° . After that the autoclave was returned to the furnace and heated overnight in the usual manner. In this way it was made certain that crystals of $\text{NaOH} \cdot \text{H}_2\text{O}$ would be present at equilibrium.

Thermocouple Calibration. Thermocouple Th. 372/370B, which had been recalibrated just prior to this series of measurements, was calibrated again near the end of them, Th. 374/370A having been used as the standard in both cases in accordance with the procedure described in Part II. In order to improve the accuracy of the temperature measurements between 60 and 65° , Th. 372/370B was calibrated at three temperatures within this range against a copper-constantan thermocouple²³ that had been calibrated at the Bureau of Standards (Test No. 62303; November, 1930). The correction to Th. 372/370B obtained by interpolation of the results of the calibration against Th. 374/370A agreed within 0.1° with that determined by this special calibration. On the basis of this agreement and the reliability of the calibration of a copper-constantan thermocouple,²⁰ we assign to the liquidus temperatures reported in Part III a maximum relative uncertainty of $\pm 0.2^\circ$, and a maximum uncertainty of $\pm 0.3^\circ$ with respect to the thermodynamic temperature scale.

Determination of Sodium. Analysis of the filtrate was started by dissolving it in CO_2 -free water (prepared by passing CO_2 -free air through boiling distilled water for half an hour) and diluting the solution until it contained approximately 3.93 per cent Na^+ . This concentration was chosen because 10 ml. of such a solution yield 1 g. of NaCl after neutralization. The total amount of solution was weighed to ± 1 mg.

For the determination of sodium two 10-gram samples of solution were weighed from a weight burette into 30-ml. platinum evaporating crucibles with flared tops. To each were

²³ We are indebted to R. E. Gibson of this Laboratory for the loan of this thermocouple.

added 3 ml. of concentrated HCl. Each solution was evaporated on a steam bath to about one-fourth its original volume. The evaporation was interrupted while another 3-ml. portion of concentrated HCl was added to each (whereupon fine crystals of NaCl were precipitated), and then it was continued to dryness. The crucibles were placed in a furnace preheated to slightly over 100°. The temperature was raised to 600° in the course of an hour and was maintained there for two hours. The crucibles were weighed after having been cooled in a desiccator for 30 minutes. The percentage of Na₂O in the original filtrate was computed from the mean amount of NaCl found.

Drying of Sodium Chloride during Analysis. At the beginning of this research a series of experiments was performed to find out the best temperature at which to dry NaCl. It has been suggested³⁴ that the NaCl be heated to incipient fusion in a covered crucible. Such a procedure will give a result that is too low. We found that the volatility of NaCl at its melting point (800° C.) is so great that in a covered crucible heated in an electric furnace the loss on fusion of previously fused NaCl amounts to at least 0.2 mg.

After having tried a number of different temperatures, we chose 600° for the final drying because it is high enough to dehydrate NaCl completely in two hours, but low enough so that there is no loss by sublimation from a covered crucible.

Determination of Carbon Dioxide. The determination of CO₂ was made in a gas-evolution type of apparatus by neutralization of the solution with dilute H₂SO₄. The evolved CO₂ was absorbed in "ascarite," after having been dried by concentrated H₂SO₄ and "anhydrone." Two separate determinations were made whenever sufficient solution remained after the sodium determinations.

Weighing. Weighings of the weight burette containing the solutions for the sodium determinations, of the evaporating crucibles containing NaCl, and of the absorption tubes containing CO₂ were made by the method of substitution on a Ruetprecht balance. The rest point could be estimated to ± 0.05 mg., as proved by a series of ten weighings of an empty platinum crucible. The weights had been calibrated with an uncertainty of ± 0.05 mg. by the method of Richards.³⁵

³⁴ For example, see Hillebrand, W. F., and Lundell, G. E. L.: *Applied inorganic analysis*; Wiley, New York, 1929, p. 521.

³⁵ Richards, T. W.: *J. Am. Chem. Soc.*, 22, 144-9, 1900.

TABLE I.
Liquidus Temperatures and Compositions.

Expt. No.	Temperature ^a Equilibrium	Initial	Stirring ^a (hours)	Gross Comp. ^b Na ₂ O CO ₂		Composition of Filtrate ^c Na ₂ O CO ₂	
<i>Solid Phases: NaOH.H₂O and Na₂CO₃</i>							
104	60.1°	59.5°	6.2	49.8%	0.34%	48.75%	0.116%
129	62.0	59.5	6.0	50.6	0.55	49.61	*0.152
106	63.1	63	5.3	51.16	*0.120
128	*63.9	64.1	7.1	51.4	0.55	51.27
107	*64.4	63	6	51.78	0.116
124	*64.7	64.2	5.7	52.0 ^d	0.55	52.24
120	64.5	56	5.9	52.5	0.54	53.34 ^e	*0.133
113	*64.7	64.5	4.1	52.9	(Analysis of residue—no filtrate.)		
122	*64.9	64.7	4.3	53.3	(Analysis of residue—no filtrate.)		
119	*64.9	63.4	5.5	52.7 ^f	0.55	53.72
115	64.8	64.6	5.2	53.6	0.55	54.67 ^g	0.206 ^h
111	64.4	63.9	6.3	54.0	0.55	55.17	0.159
101	*63.4	62.9	6.0	54.6	0.35	55.94	0.158
110	*62.3	68.7	11.5	54.6	0.55	55.39 ^e	0.155
114	62.4	62.6	6.5	54.5	0.55	56.57
103	62.6	62.4	5.0	55.7	0.26	56.63	*0.132
<i>Solid Phases: NaOH and Na₂CO₃</i>							
93 ^h	60.2	60.4	4.3	56.6	0.16	56.46
112 ^h	61.4	66.5	10.8	58.1	0.57	56.59	0.159
97	62.6	62.7	5.0	60.4	0.17	56.60
91	64.9	68.9	10.3	62.2	0.15	56.73	*0.107
92	65.1	61.6	8.5	62.2	0.15	56.75	*0.106
89	69.8	88	10.3	62.7	0.21	56.92	*0.144
90	69.9	65.2	8.9	62.2	0.15	56.99	*0.127

^a The *initial temperature* was that at the beginning of stirring. The period of *stirring* was the total time; during the last 4.0 hr. of stirring, the temperature was maintained at the *equilibrium* value. When the equilibrium temperature is preceded by an asterisk, the observed variation from the mean was $\pm 0.05^\circ$; in all other experiments it was $\pm 0.1^\circ$. The relative uncertainty, however, as already mentioned, was $\pm 0.2^\circ$ in all cases, because of the uncertainty in the thermocouple calibration.

^b The *gross composition* of each mixture (except in Expts. 113 and 122) was computed from the known composition of the ingredients; but each value for Na₂O may be too small by as much as one per cent because of loss of water by evaporation during mixing of the ingredients.

^c Each Na₂O percentage listed under *composition of filtrate* is the mean of duplicate determinations. Each has been corrected for non-volatile matter in the HCl used in the analysis (correction, -0.003 per cent); and for air buoyancy (correction, -0.01 per cent). The probable error was taken as the square root of the sum of the squares of (1) the mean deviation of the two determinations; (2) the systematic error in the weight calibration; and (3) an estimated systematic error of ± 0.005 per cent in the correction for air buoyancy. The absolute magnitude of the individual probable errors ranges from ± 0.008 per cent (Expts. 107 and 120) to ± 0.044 per cent (Expt. 89), the root mean square error for the 21 experiments being ± 0.021 per cent.

Each CO₂ percentage marked with an asterisk is the mean of duplicate

EXPERIMENTAL DATA.

The information gained from a single experiment was the composition of the liquid in equilibrium with two solid phases— Na_2CO_3 and either NaOH or $\text{NaOH}\cdot\text{H}_2\text{O}$ —at a measured temperature. Because the NaOH pellets contained slightly more Na_2CO_3 than such a doubly saturated solution between 60 and 70° , it was not possible to make experiments with solutions in the $\text{NaOH}\cdot\text{H}_2\text{O}$ field containing less than the saturation amount of Na_2CO_3 . In order to be certain that the reaction mixture contained an abundance of solid Na_2CO_3 at equilibrium, a small amount of $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ was added to it, except in the first few experiments.

The composition of the liquid at equilibrium is listed for each experiment in Table I. In several cases there was sufficient solid phase to form a mush that did not flow easily through the hole in the bottom of the reaction chamber into the filter crucible; with the result that there was not sufficient filtrate⁸⁶ for a CO_2 determination. * Because of the small CO_2 content of these filtrates, between three and four grams of filtrate were needed for analysis in order that five milligrams of CO_2 might be weighed.

The lack of complete data on the CO_2 content of the filtrate does not seriously affect the value of these solubility determinations; because the CO_2 content is both small and practically independent of the temperature along the boundary between the $\text{NaOH}\cdot\text{H}_2\text{O}$ and Na_2CO_3 fields above 60° . There seems to be a tendency for a maximum CO_2 content at the maximum temperature; but it is not well-defined. The occurrence of such a maximum would not be surprising, for it would mean merely that in the ternary diagram the boundary between the $\text{NaOH}\cdot\text{H}_2\text{O}$ and Na_2CO_3 fields curves around the melting point

⁸⁶ In Experiments 113 and 122 no filtrate at all was obtained for the same reason. Analysis of a sample of the residue in the reaction chamber fixed a point above which the liquidus temperature must lie at that particular Na_2O content. The results of these two experiments are in agreement with the other results.

determinations. The deviation from the mean ranges from ± 0.001 per cent (Expt. 106) to ± 0.007 per cent (Expt. 91), the root mean square deviation for the 8 experiments being ± 0.005 per cent.

^d Analysis of residue in reaction chamber: 52.77 per cent Na_2O .

^e No solid phase present because of undercooling. See text, p. 210.

^f Analysis of residue in reaction chamber: 53.62 per cent Na_2O .

^g Results may be a little too high, because platinum felt in filter crucible disintegrated at end of this experiment.

^h NaOH metastable.

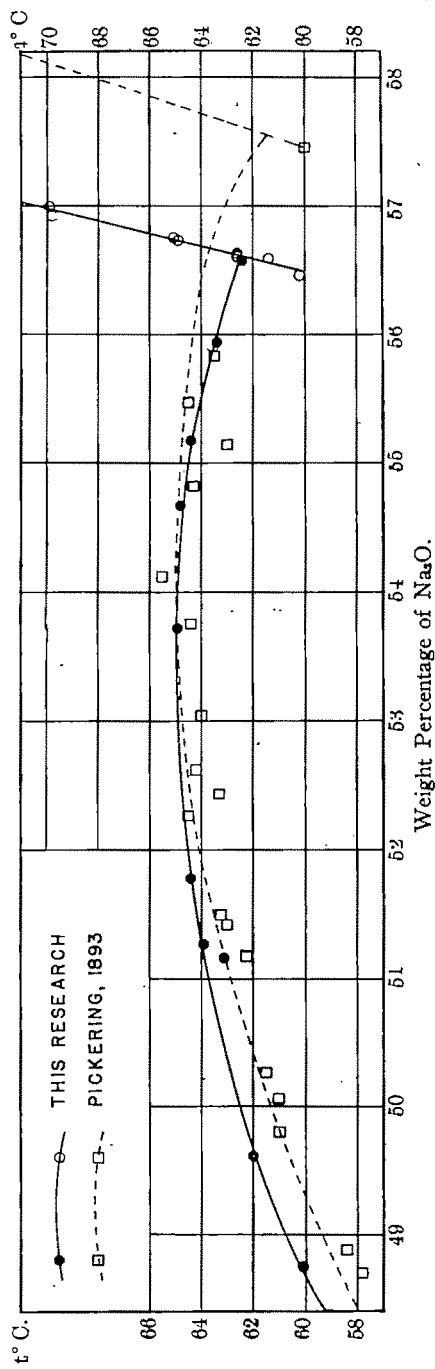


Fig. 2. Na_2O content along the boundary between the Na_2CO_3 field and the $\text{NaOH}\cdot\text{H}_2\text{O}$ and NaOH fields in the system $\text{NaOH}-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$.

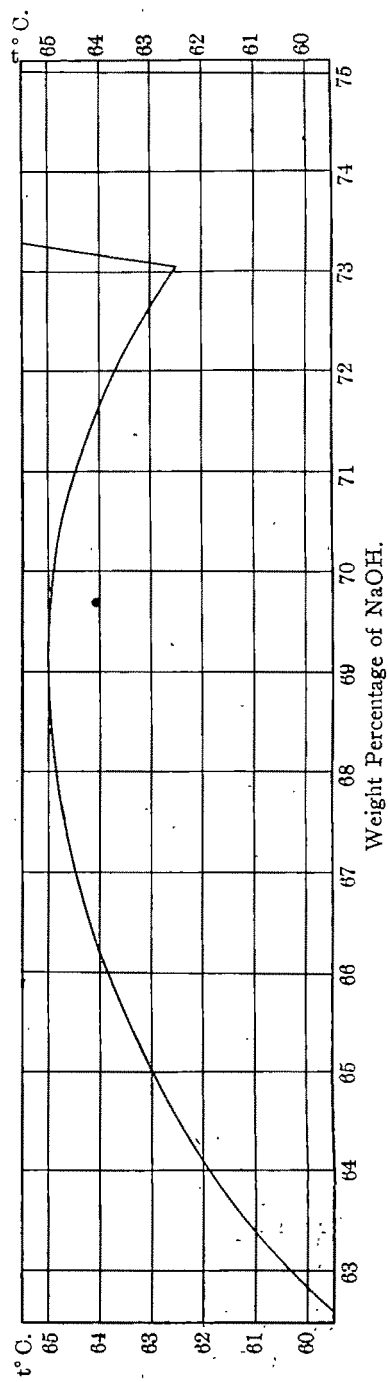


Fig. 3. Solubility of NaOH in water (solution saturated with CO_2 and total alkali computed as NaOH).

of $\text{NaOH} \cdot \text{H}_2\text{O}$. In the absence of more precise information, however, the best we can do is to suggest 0.14 ± 0.04 per cent as the most probable value of the CO_2 content along this boundary curve above 60° . Along the boundary between the NaOH and Na_2CO_3 fields, our data are adequate.

Na_2O Content as a Function of Temperature. The values of the Na_2O content (except for that in Expt. 106) are very self-consistent, as shown in Fig. 2 by the way they fall on a smooth curve. This curve gives the Na_2O content as a function of the temperature along the boundary between the Na_2CO_3 field and the $\text{NaOH} \cdot \text{H}_2\text{O}$ and NaOH fields of the liquidus surface.

The point of maximum temperature along the curve must occur at the composition determined by the intersection of the $\text{NaOH} \cdot \text{H}_2\text{O}$ — Na_2CO_3 join and the boundary curve between the $\text{NaOH} \cdot \text{H}_2\text{O}$ and Na_2CO_3 fields in a ternary diagram. Assuming a CO_2 content of 0.14 per cent along the boundary curve (see above), the corresponding Na_2O content has been computed⁸⁷ analytically to be 53.45 per cent. In drawing the curve in Fig. 2, the maximum was made to occur at this composition, the maximum temperature having been determined by the shape of the curve itself as fixed by the experimental results. It is $65.0 \pm 0.5^\circ \text{C}$.

Ternary Eutectic. The position of the ternary eutectic between $\text{NaOH} \cdot \text{H}_2\text{O}$, NaOH , and Na_2CO_3 is indicated in Fig. 2 at a temperature of $62.5 \pm 0.5^\circ \text{C}$. and a Na_2O content of 56.60 ± 0.05 per cent. Linear extrapolation of the CO_2 content along the boundary between the NaOH and Na_2CO_3 fields (Expts. 89, 90, 91, and 92, Table I) gives 0.093 per cent at 62.5° . This is a little lower than that indicated by the determinations (especially Expt. 103) along the $\text{NaOH} \cdot \text{H}_2\text{O}$ curve. We select 0.11 ± 0.02 per cent as the mean CO_2 content at the ternary eutectic. The H_2O content, by difference, is 43.29 per cent. When the components are changed, this same composition becomes: NaOH , 72.85 ± 0.10 per cent; Na_2CO_3 , 0.27 ± 0.05 per cent; and H_2O , 26.88 ± 0.15 per cent.

Comparison with Data of Pickering. The points determined by Pickering⁸⁸ also have been plotted in Fig. 2, together with the smooth curve that he had drawn through them. Pickering had recorded his data as the percentage of NaOH in a solu-

⁸⁷ For the method of computation, see Morey, G. W.: *J. Phys. Chem.*, 34, 1745-50, 1930.

⁸⁸ Reference (30): Table I, p. 900; Fig. 1, facing p. 890.

tion whose freezing point he measured; but in the absence of any reference to efforts made to prepare CO_2 -free NaOH or to work in a CO_2 -free atmosphere, we assume that actually he measured the freezing points along the $\text{NaOH} \cdot \text{H}_2\text{O}$ — Na_2CO_3 boundary. For plotting his data, we have converted his recorded NaOH percentages to Na_2O percentages by multiplying by the factor 0.7748.

Although the reproducibility of Pickering's measurements was not as great as that of ours, it was remarkably good in view of the simple experimental method that he had used—merely a thermometer in a test tube. The portion of his measurements reproduced in Fig. 2, however, seems to have been affected by a systematic error in the determination of the composition of the solutions. Although he reported the same maximum temperature that we have found, the composition at this temperature was 54.2 per cent Na_2O instead of 53.45 per cent. Similarly for corresponding temperatures throughout the curve, the composition he reported was greater³⁹ than that which we have found. That Pickering's results rather than our own are in error is established by the fact that shifting the maximum of his curve to the theoretical percentage⁴⁰ of 53.45 per cent Na_2O would cause disagreement between the curve and his experimentally determined points.

Comparison with Data of Dietz. The difference just noted between our data and those of Pickering is the same as that between his data and those of Dietz⁴¹ throughout the course of the solubility curve of $\text{NaOH} \cdot \text{H}_2\text{O}$. A direct comparison between our data and those of Dietz is possible only at the maximum on the solubility curve, for his next highest temperature was 53° , and the curvature of the curve is too great to permit accurate interpolation. Dietz placed the maximum temperature at $64 \pm 1^\circ$, and we have placed it at $65.0 \pm 0.5^\circ$, at the same composition, which is good agreement.

Undercooling. Experiments 110 and 120 are interesting because they illustrate the ease of undercooling a solution that

³⁹ The difference cannot be ascribed to a difference in atomic weights; for Pickering mentioned (p. 894) that $\text{NaOH} \cdot 3\text{H}_2\text{O}$ contains 42.55 per cent NaOH , and the percentage on the basis of the 1938 International Atomic Weights is 42.53 per cent.

⁴⁰ If Pickering really measured the solubility of NaOH in water in the absence of CO_2 , the maximum of the curve should have been at 53.43 per cent Na_2O (or at 69.0 per cent NaOH , instead of at 70.0 per cent as shown on his graph).

⁴¹ See p. 202.

has a composition close to that of $\text{NaOH} \cdot \text{H}_2\text{O}$, provided that all crystals of $\text{NaOH} \cdot \text{H}_2\text{O}$ have been melted.

In Expt. 110 the reaction mixture was placed in the autoclave that had been preheated to about 65° , and then was heated overnight to 68.7° . In the morning it was cooled with stirring to the equilibrium temperature of 62.3° , and kept there for 4.0 hours before filtration. No solid material remained in the reaction chamber after filtration; and the composition of the filtrate was not far from that of the starting material. Contrasted with this result was that shown in Table I for Expt. 114, which was a duplicate experiment except that crystals of $\text{NaOH} \cdot \text{H}_2\text{O}$ were formed by a preliminary freezing after the reaction mixture had been dissolved.

In Expt. 120 the usual procedure was modified as follows. The reaction mixture was placed in the autoclave that had been preheated to about 60° , and stirring was started immediately. After 0.9 hr. the temperature had reached 64° , and at the end of 2.0 hr. it had reached 64.5° . It was maintained at $64.5 \pm 0.05^\circ$ for 4.0 hr., after which the diaphragm was cut and the mixture was filtered. No solid material remained in the reaction chamber after filtration; and again the composition of the filtrate was close to that of the starting material. Apparently all the NaOH had dissolved to form a solution from which no $\text{NaOH} \cdot \text{H}_2\text{O}$ crystallized because the solution never was undercooled sufficiently.

Further evidence of the reluctance of $\text{NaOH} \cdot \text{H}_2\text{O}$ to crystallize was observed in several experiments near the ternary eutectic. After a reaction mixture had been dissolved by stirring in the autoclave at about 65° , it was cooled slowly with stirring until it froze. Table II gives the temperature at which freezing started when the solution was cooled at the rate of a few tenths of a degree a minute. The solid phase that appeared

TABLE II.
Undercooling of Solutions of NaOH .

Expt.	Gross Composition	Minimum Temperature	Undercooling
92	62% Na_2O	55.9°	6.6°
93	56%	57.4°	5.1°
95	62%	57.0° ; 55.0°	5.5° ; 7.5°
96	57%	51.4°	11.1°
100	55%	51° ^a	11.5°

^a Solution not stirred during cooling.

in Expt. 93 must have been NaOH, judging from the composition of the filtrate that was obtained (see Table I), for the mixture had not been heated above 60.4° after it had melted. In the other experiment (Expt. 112) along the metastable prolongation of the solubility curve for anhydrous NaOH the reaction mixture first was stirred at 66.5° and then was cooled to the equilibrium temperature of 61.4°.

EXTRAPOLATION OF THE SOLUBILITY DATA.

A saturated solution of NaOH between 60 and 70° will be saturated also with respect to Na_2CO_3 , unless some special process is employed for making the solution from NaOH that truly is carbonate-free. Hence it is of no practical importance that our data concerning these solutions cannot be extrapolated

TABLE III.
Composition of Solutions Saturated with Respect to
 Na_2CO_3 and $\text{NaOH} \cdot \text{H}_2\text{O}$ or NaOH.

Temp. ^a (° C.)	Na_2O (wt. pct. $\pm 0.03\%$)	Total alkali computed as NaOH (wt. pct. $\pm 0.05\%$)	NaOH (wt. pct. $\pm 0.1\%$)	Na_2CO_3 (wt. pct. $\pm 0.05\%$)	Solid Phases ^b
60.0	48.67	62.81	62.5	0.35	A & C
61.0	49.10	63.37	63.1	0.35	A & C
62.0	49.66	64.09	63.8	0.35	A & C
63.0	50.37	65.01	64.7	0.35	A & C
64.0	51.29	66.19	65.9	0.35	A & C
65.0	53.45	68.98	68.7	0.35	A & C
64.0	55.50	71.63	71.4	0.35	A & C
63.0	56.27	72.62	72.4	0.30	A & C
62.5	56.60	73.05	72.8 ₅	0.27	A, B, & C
63.0	56.63	73.09	72.9 ₀	0.27	B & C
64.0	56.68	73.15	72.9 ₅	0.28	B & C
65.0	56.74	73.23	73.0 ₀	0.29	B & C
70.0	56.97	73.53	73.3 ₀	0.33	B & C

^a This temperature scale is only relative. A temperature may differ from the thermodynamic scale by $\pm 0.5^\circ$ at a particular composition.

^b Solid phases: A = $\text{NaOH} \cdot \text{H}_2\text{O}$; B = NaOH; and C = Na_2CO_3 .

to the border of the ternary diagram to yield the true solubility of NaOH in water. That temperature-solubility curve presumably would not be far different from that which we have obtained for the doubly saturated solution; although the maximum temperature (which would be the true melting point of NaOH.H₂O) might be raised by as much as five degrees by the absence of carbonate, although such a large change is not likely.

Instead of attempting an extrapolation based on insufficient evidence,—and the work required to secure more evidence would scarcely be justified,—we have prepared a table (Table III) that shows the composition of the doubly saturated solutions as actually encountered in laboratory practise. The first column of the table gives the Na₂O content as read from the smooth curve in Fig. 2. The second column gives the total alkali content of the solutions computed as NaOH by multiplying the percentage of Na₂O by 1.2906. These values are shown graphically in Fig. 3. The third and fourth columns of Table III give the amounts of the separate alkalis in the saturated solutions, as computed from the Na₂O content and the CO₂ content.

OPTICAL PROPERTIES OF NaOH AND OF NaOH.H₂O.

The phase relations were so simple in the part of the system, NaOH—Na₂CO₃—H₂O, that we have investigated, that it was not necessary to make optical examinations in order to identify the solid phases present at equilibrium. But since the optical properties of neither NaOH nor its monohydrate have been published heretofore, we thought this an appropriate time to do so. Our colleagues Dr. Merwin and Dr. Ingerson kindly consented to make the examinations. The results they obtained are presented in Table IV.

SUMMARY.

We have made a precise determination of the position of the boundary between the field of Na₂CO₃ and the fields of NaOH.H₂O and NaOH in the ternary system, NaOH—Na₂CO₃—H₂O, in the temperature range 60 to 70°. The liquidus temperature varies little as long as NaOH.H₂O is the solid phase along with Na₂CO₃, reaching a flat maximum of 65° at 53.45 per cent Na₂O. The ternary eutectic is at 62.5° and 56.60 per cent Na₂O. From this point the temperature

TABLE IV.
Optical Properties of NaOH and of NaOH.H₂O.

	NaOH ^a	NaOH.H ₂ O ^b
Crystal system	Orthorhombic (or pseudo-orthorhombic?) ^c	Orthorhombic (or monoclinic?) ^c
Habit and orientation	Blades: flattened \parallel (001) Plates: flattened \parallel (001) Nearly equant grains	Blades: flattened \parallel (001), elongated \parallel <i>a</i> , and terminated by (110) and (110) and by (110) and (110) at interior angle of $92 \pm 2^\circ$. Edges frequently beveled by slightly developed domal and pyramidal faces
Cleavage	Eminent, \parallel (001) Imperfect, \parallel (110), angles about 90°	Good, \parallel (001)
Color	Colorless	Colorless
Extinction	Extinction directions on cleavage flakes nearly or quite bisect the angles of the other cleavages	Parallel to elongation
Refractive indices and	$\left\{ \begin{array}{l} \alpha(?) = 1.45_7 \\ \beta(?) = 1.47_0 \\ \gamma(c) = 1.47_2 \end{array} \right.$	$\left\{ \begin{array}{l} \alpha(c) = 1.435 \pm 0.004 \\ \beta(a) = 1.470 \pm 0.004 \\ \gamma(b) = 1.475 \pm 0.004 \end{array} \right.$
Optical orientation		
Optical character	Biaxial negative	Biaxial negative
Optic axial angle	$2V = 50 \pm 10^\circ$	$2V = 45 \pm 5^\circ$
Dispersion of optic axes	None apparent
Interference figure	Cleavage flakes normal to obtuse bisectrix	Cleavage flakes normal to acute bisectrix

^a Examination by H. E. Merwin.^b Examination by Earl Ingerson.^c The probability that this substance is not orthorhombic is very slight.

Remarks on the Optical Examinations. Three types of crystalline NaOH were studied. Radiating blades were obtained by melting and quenching the nearly pure hydroxide. Plates and nearly equant grains, which had grown in aqueous solutions at 270° in the course of solubility determinations, were obtained as lumps cemented together by solidified mother liquor. Powdering the lumps under paraffin oil to secure clean surfaces was accompanied by deformation and the development of strain-birefringence. Cutting or chopping with a sharp scalpel gave the best fragments. Interference figures obtained from fragments cut normal to the cleavage showed marked effects of distortion. Because of the ease of deformation of the crystals, the optical properties

risks rapidly with increase of Na_2O content, NaOH being the second solid phase.

As a demonstration of the worth of the new type of filter autoclave for solubility measurements that was described in Part II of this paper, these experiments were very satisfactory. Even close to the maximum of the solubility curve it was possible to make determinations by careful control of the gross composition of the reaction mixture. For the determination and composition of the ternary eutectic, the autoclave was especially well suited.

The optical properties of NaOH and $\text{NaOH}\cdot\text{H}_2\text{O}$ have been measured by H. E. Merwin and Earl Ingerson, respectively, using samples that we prepared.

This study, which is part of a comprehensive research program concerning water in alkali silicate melts, has been aided by means of special funds made available to the Carnegie Institution of Washington by the Carnegie Corporation of New York.

could not be measured as accurately as otherwise would have been possible; and for the same reason it could not be determined whether the optic axes are dispersed. It was noticed that the crystals themselves were more dispersive than the paraffin oils used as immersion media.

The $\text{NaOH}\cdot\text{H}_2\text{O}$ that was examined consisted of residues from several of the experiments near the melting point. In the measurement of the refractive indices and in the study of the interference figures, the flakes of $\text{NaOH}\cdot\text{H}_2\text{O}$ were crushed under oils to secure fresh surfaces. In the study of the crystal habit, crystals were grown in aqueous mother liquor in a shallow glass cell on the microscope stage.

THE SYSTEM, WATER—SODIUM DISILICATE

G. W. MOREY AND EARL INGERSON.

ABSTRACT.

An apparatus has been constructed for studying the lowering of melting point of silicates when heated in steam at high pressures, and the results of a study of the system, water—sodium disilicate, are presented.

Water is an essential constituent of rock magmas, in which it exerts a profound effect both on physical characteristics such as viscosity and especially on the crystallization phenomena, which it affects not only by lowering the temperature of separation of crystalline minerals but also by determining the composition of the minerals which separate. In addition, the concentration of water in the crystallizing magma affords a source of internal pressure¹ which increases as cooling and consequent crystallization progress, up to the region of maximum pressure.

The study of the effect of water on mineral formation, the hydrothermal synthesis of minerals, owes its beginning largely to the French investigators Daubrée, St. Claire Deville, and Friedel and Sarasin. The voluminous literature of the subject has recently been critically summarized by Morey and Ingerson,² who point out that almost all the published work deals with the synthesis of silicate minerals by heating their components in closed vessels under conditions frequently not given and never either resembling the conditions found in nature or approximating to the equilibrium conditions in the systems under investigation. Clearly such studies are of little more than passing interest. There is need for the development of systematic information leading to a knowledge of the part played by water in silicate equilibria; of the phase equilibrium relationships in systems containing both water and silicates. Only on such information can be based a competent theory of the chemistry of the processes of magmatic differentiation, of mineral formation, and ore deposition.

The simplest systems that are pertinent to the problem are those binary and ternary systems containing water and silicates of the alkali metals. A beginning of such a study was made

¹ Morey, G. W.: *J. Wash. Acad. Sci.*, 12, 219, 1922; *J. Geol.*, 32, 291, 1924.

² Morey, G. W., and Ingerson, Earl: *Econ. Geol.*, 32, 607, 1937.

by Morey and Fenner³ with the system, water—potassium metasilicate—silica, which was made possible by the fortunate circumstance that over a wide range of composition the solutions formed could be quenched and the equilibria frozen by chilling the steel bomb used as a container. Such a method is not generally applicable, and a more powerful one had to be devised.

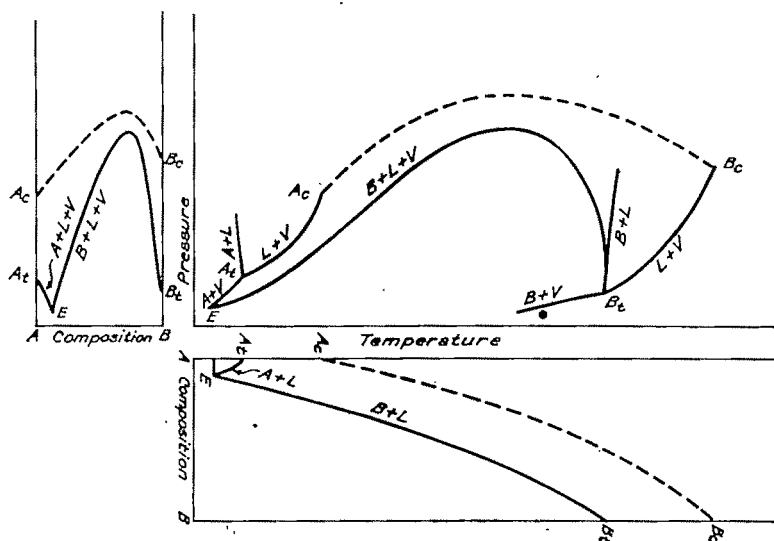


Fig. 1. Projections on the temperature-concentration, temperature-pressure, and pressure-concentration planes of a solid model which gives a diagrammatic representation of the phase equilibrium relationships in a binary system with components of widely different volatility, in which the critical or plait point curve is not intersected by the solubility curve. A_t and A_c , and B_t and B_c , represent the triple and critical points for the two components, respectively. E is the binary eutectic.

The new method, and its application to a simple binary system, are described below.

The theory of systems containing volatile components such as water together with non-volatile components such as silicates has been discussed by several authors, including Morey and Ingerson, who give references to other papers on the subject. In general the solubility or fusion curve is continuous from the eutectic or cryohydrate temperature to the melting point of the non-volatile component, although there are complications when

³ Morey, G. W., and Fenner, C. N.: J. Am. Chem. Soc., 39, 1173, 1917.

critical end-points are met with or if the components become immiscible. For our present purpose these complications may be ignored, and discussion confined to the simple case illustrated diagrammatically in Fig. 1, in which are shown the projections of the solid P — T — X model on the temperature-concentration (T — X), pressure-temperature (P — T), and pressure-concentration (P — X) planes. In the T — X diagram, the temperature falls along the three-phase curve, $B + L$, which gives the simultaneous values of temperature and composition in the univariant system, solid + liquid + vapor. The freezing point of B is lowered on addition of the component of greater volatility until the eutectic E is reached. In the corresponding P — T projection are shown values of the vapor pressure of the solutions of composition given in the T — X diagram. It will be observed that the vapor pressure of these solutions first rises to a maximum as temperature is lowered, then falls to the eutectic at E . In the P — X projection are shown corresponding values of composition and vapor pressure. The steep rise of the curve is a usual characteristic of such systems.

We are especially interested in the upper part of the solubility curve, that is, in the lowering of freezing point of silicates on addition of water, and the relation between this lowering of freezing point and pressure. In order to investigate this we have constructed an apparatus which makes it possible to apply to meltings made in an atmosphere of steam at high pressures the "quenching method" so extensively used in the Geophysical Laboratory. By making a series of quenches under a constant pressure of steam, the freezing point of the solution at that temperature can be determined, and from a series of such measurements at constant pressure the P — T curve can be determined. Analysis of the quenches just at the liquidus gives the composition of the solution, and thus enables the determination of the three variables, pressure, temperature, and composition. It should be emphasized that in these experiments we are interested only in the saturation surface representing coexistence of solid, liquid, and vapor, not in the effect of pressure on melting point in the absence of vapor. The apparatus and method are evidently capable of solving many problems in this unexplored field. Our present study is confined to the system, H_2O — Na_2O — SiO_2 , and in this paper the results will be restricted to the P — T curve of the binary system, H_2O — $Na_2O.SiO_2$.

The construction of the apparatus is illustrated by the dia-

TABLE I.
 $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ in Steam up to 2000 lb./sq. in..

Run	Pressure lb.	Temp. ° C.	Time	Result
1	200	828.2	20 min.	Slightly sintered; crystalline.
2	200	843.3	20 min.	Glassy rim; crystals in center; not enough time.
3	200	843.3	30 min.	Top frothed; bottom glassy with crystals; not enough time.
4	200	835.1	2 hrs.	Glassy.
5	200	831.6	2½ hrs.	Glassy rim; crystals in center.
6	200	829.6	18 hrs.	Glassy rim; crystals in center.
1	500	784.9	6 hrs.	Sintered; crystalline.
2	500	807.7	4 hrs.	Sintered; crystalline.
3	500	819.1	16 hrs.	Glassy; frothed.
4	500	813.4	16 hrs.	Glassy; frothed.
5	500	810.9	16 hrs.	Sintered; crystalline.
6	500	812.4	12 hrs.	Glassy; center frothed.
7	500	811.9	20 hrs.	Glassy; frothed.
1	1000	805.4	16 hrs.	Glassy; top frothed.
2	1000	793.8	18 hrs.	No quench; frothed; probably above liquidus.
3	1000	789.3	14 hrs.	Glassy; top frothed.
4	1000	757.5	6 hrs.	Sintered; crystalline.
5	1000	773.1	20 hrs.	Sintered; crystalline.
6	1000	781.5	14 hrs.	Glassy; ran out of foil.
7	1000	777.4	6 hrs.	Sintered; crystalline.
8	1000	779.3	14 hrs.	Glassy.
1	2000	746.6	16 hrs.	Glassy.
2	2000	718.4	1½ hrs.	Not sintered.
3	2000	727.3	14 hrs.	Top part frothy, but crystalline.
4	2000	732.3	1½ hrs.	Glassy.
5	2000	729.2	16 hrs.	Top frothed; center crystalline; bottom some clear glass.
6	2000	730.4	18 hrs.	Glassy; top frothed.
7	2000	730.4	14 hrs.	Glassy; frothed.
8	2000	730.4	14 hrs.	Glassy; frothed, except center.

grammatic sketch shown in Fig. 2 and a photograph of the assembly is shown in Fig. 3. The central part of the quenching furnace, F, is much like the quenching furnaces used for the study of anhydrous systems. A refractory tube, one-half inch in internal diameter and eleven-sixteenths inch external diameter, is wound with 14.5 meters of 0.6 mm. platinum—10 per cent rhodium wire, giving a resistance of 10 ohms at room temperature.

The furnace is enclosed in a gas-tight bomb of stainless steel (Carpenter No. 2), six inches in external diameter, closed at

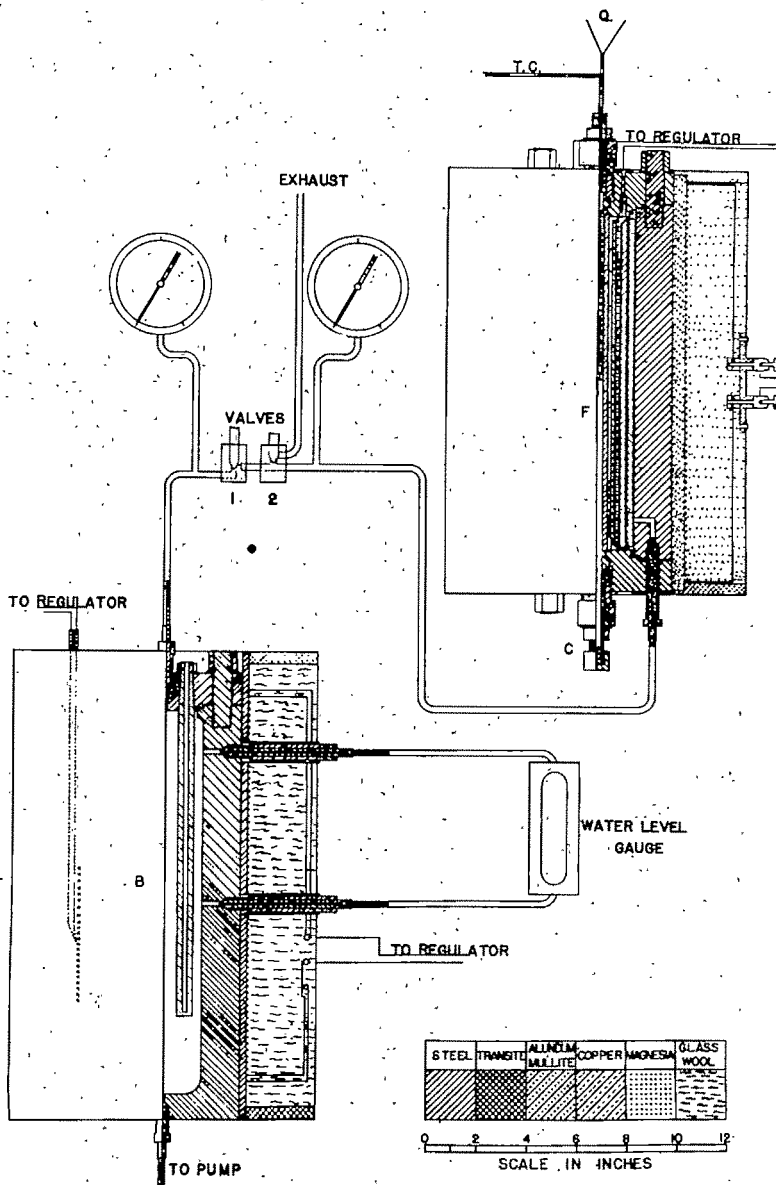


Fig. 2. Diagrammatic representation of an apparatus for quenching in steam at high pressure.

top and bottom by stainless steel covers, bolted down, and the joint made tight with a gold washer, the closure being of the



Fig. 3. Assembly of an apparatus for quenching in steam at high pressure.

type customarily used in this Laboratory. The bomb is provided with an inlet tube for the steam, and the necessary fittings for introducing the furnace leads, quenching leads and thermo-

couple wires, and for introducing and removing the charge. Between the furnace and the bomb are two cylindrical platinum baffles, one tight at the top, the other tight at the bottom, separated from each other, the bomb, and the furnace by three thick "sillimanite" tubes. This system of baffles prevents convection currents and ensures that the steam is heated to temperature before it comes in contact with the charge. Surrounding the stainless steel bomb is a furnace which serves to maintain the entire bomb at a temperature of about 500°, or lower if desired.

The charge, wrapped in platinum foil, is held in the hot spot of the high-temperature furnace by a porcelain ring suspended by a fine platinum wire from the quenching leads, Q. The quenching leads and thermocouple wires pass through limestone and talc packings in a plug fitted to the upper cover of the bomb, and made tight by a copper washer and the usual type of closure.

The temperature of the inner furnace is held constant by a Roberts wheatstone-bridge type furnace regulator, developed for that purpose at this Laboratory. The temperature of the outer furnace is controlled by a series rheostat, and requires no regulation.

Steam is generated in the boiler, B. The construction is similar to that of the bomb, except that simple cone-type high-pressure connections are used instead of the plugs necessary on the bomb. The metal is Carpenter's stainless steel No. 3. Insulation is with glass wool. A water-level gauge and a high-pressure pump make it possible to fill the boiler when it is in operation. Regulation is by means of a thermocouple placed almost against the heating coil, used in connection with a Leeds and Northrup Micromax regulator. A chromel-alumel thermocouple gives very good regulation below 270°, and above that two platinum-platinum rhodium couples in series are used.

The steam is led through a double valve and enters the bomb through the side. It thus is constrained to pass up and down through the baffle system before it enters the inner furnace tube at the bottom and comes into the hot spot of the furnace. The system of baffles has proved perfectly satisfactory in preventing fluctuations of temperature and minimizes drift of the hot spot when the pressure is changed.

The valve block contains two valves, one of which (1) separates the boiler and bomb, and the other (2) enables the bomb to be exhausted. Pressure gauges on each side of the valve

are used for general control. They are calibrated regularly against each other and against a dead-weight gauge, and during each run by measuring the temperature of the water in the boiler and comparing with steam tables.

The details of a run with this apparatus are as follows. A charge of about 20 milligrams of anhydrous material, wrapped in platinum foil, is suspended from the quenching leads. It makes little difference whether the initial material is crystalline or glassy. The plugs are tightened, and the temperature and pressure are brought to the desired values and maintained long enough for equilibrium to be reached. A heavy current is then passed through the quenching leads, *Q*, melting the fine wire supporting the charge, which drops into the quenching cup, *C*. The temperature of this cup is kept slightly above that of the boiler by means of a small supplementary heater, not shown.

The steam is then blown off by opening the exhaust valve after closing the intermediate valve. The screw cap is removed from the cup, and the charge taken out and examined with the petrographic microscope, to ascertain if it is all glassy and hence was above the liquidus. If the charge is found to contain some crystals, these are identified by determining their optical properties.

By a series of such quenches at constant pressure, with initial anhydrous material of the same composition, the liquidus at that pressure can be obtained; and by repeating at a series of pressures and a series of compositions of anhydrous materials, the entire system within the range of the apparatus can be worked out with certainty and precision comparable to those obtained in anhydrous quenches. Below the critical point of water the boiler used affords the most convenient source of water pressure, and the precision with which the vapor pressure curve of water is known gives an exact knowledge of the pressure. At higher pressures dependence must be placed on gauges.

We have investigated in the manner described above a part of the system, $\text{H}_2\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$. Anhydrous melts of several compositions have been prepared and the liquidus temperatures determined at one or more pressures. In only one case, sodium disilicate, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, has a series of experiments at various steam pressures been completed. These are summarized in Table I. Fig. 4 shows the *P-T* diagram for the part of the binary system, $\text{H}_2\text{O}-\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, which has been studied

The pressure increases more rapidly as the temperature falls, a circumstance to be expected from thermodynamic considerations in systems in which the volatile component is far above its critical temperature and is only slightly soluble. The maximum pressure has not been reached. It will be recalled that in the system, $\text{H}_2\text{O}-\text{K}_2\text{O} \cdot 2\text{SiO}_2$, the maximum was at about 75 atmospheres pressure, 600° , and 4 per cent H_2O by weight.

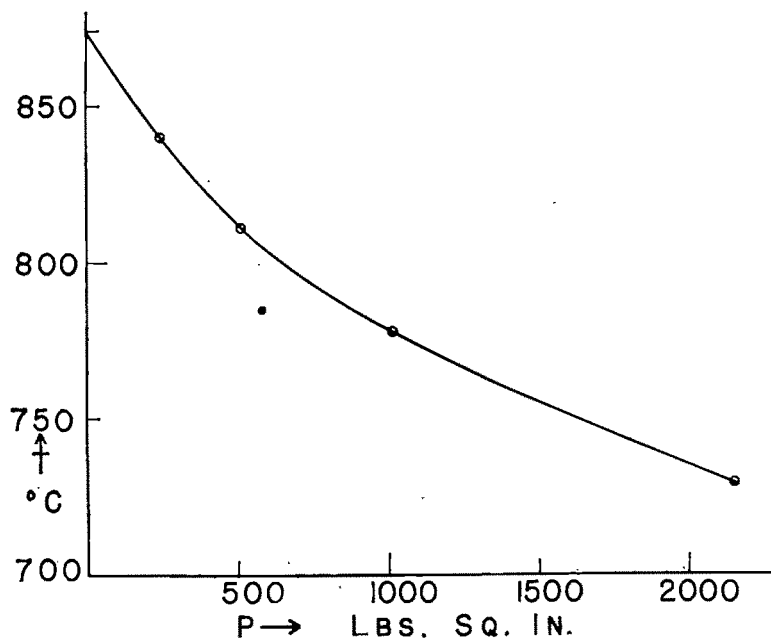


Fig. 4. Pressure-temperature diagram for solid-liquid-vapor equilibrium in the system, $\text{H}_2\text{O}-\text{Na}_2\text{O} \cdot 2\text{SiO}_2$.

The possibility of an appreciable volatilization of sodium oxide with steam at high pressure was of interest, and experiments were made with sodium metasilicate, $\text{Na}_2\text{O} \cdot \text{SiO}_2$, to find if there was any change in composition under rather extreme conditions. No change could be detected.

This study, which is part of a comprehensive research program concerning water in alkali silicate melts, has been aided by means of special funds made available to the Carnegie Institution of Washington by the Carnegie Corporation of New York.

RADIUM IN ROCKS: V. THE RADIUM CONTENT OF THE FOUR GROUPS OF PRE-CAMBRIAN GRANITES OF FINLAND.

CHARLES SNOWDEN PIGGOT.

ABSTRACT.

The radium content of the pre-Cambrian granites of Finland is reported, grouped according to the four classifications of Sederholm.

The pre-Cambrian granites of Finland are some of the oldest rocks available, and the fact that they have been so thoroughly mapped and classified makes them particularly useful for study. The Geological Survey of Finland, under the direction of Dr. J. J. Sederholm,¹ has conducted a very exhaustive survey of these rocks, mapped them geologically, and classified them according to several pre-Cambrian "cycles of sedimentation" into four great subdivisions.

In the summer of 1932, Dr. Tom. F. W. Barth, then a member of the staff of the Geophysical Laboratory, visited Finland and, with Doctor Sederholm's assistance, selected several representative samples of each of these four subdivisions. The radium content of the samples, arranged according to the Sederholm grouping, is given below:

GROUP I.

The oldest granites in Finland, called "gneissose or post-Svionian granites."

Serial No.

P-71 Granite from Bockholm, Enklinge, in the Åland Archipelago.*

P-72 Gneissose granite from Pävskär, about 40 km. west of Helsingfors.*

P-73 Gneiss-granite (Vätskär type) from Bergholm, east of Pellinge, 80 km. east of Helsingfors.*

P-74 Granite from the western shore of Orijärvi.*

¹ Cf. Sederholm, J. J.: Pre-Quaternary rocks of Finland, Bull. comm. géol. Finlande, No. 91, 1930; The geology of Fennoscandia, *ibid.*, No. 98, 1932.

* Sederholm, J. J.: On migmatites, etc., Part III, Bull. comm. géol. Finlande, No. 107, 1934.

* Sederholm, J. J.: On migmatites, etc., Part II, Bull. comm. géol. Finlande, No. 77, 1926.

* Sederholm, J. J.: On migmatites, etc., Part I, Bull. comm. géol. Finlande, No. 58, 1923.

* Eskola, P.: On the petrology of the Orijärvi region in southwestern Finland; Bull. comm. géol. Finlande, No. 40, 1914.

Radium content of Group I.

Serial No.	Grams $\times 10^{-12}$ Ra per gram rock
P-71	1.04
P-72	0.63
P-73	0.85
P-74	1.23

GROUP II.

Younger Archean coastal granites. Post-Bothnian granites.

Coastal

Serial No.

- P-75 From Kumlinge, Åland Archipelago. Post-Bothnian penetrating the gneissose granite of P-71.⁶
 P-76 From Ingå, about 40 km. west of Helsingfors.⁸
 P-79 Helsinkite granite from Kajholmen, about 20 km. east of Helsingfors.

Interior

- P-80 From Lavia.⁷
 P-81 From Siuro (highway between Tampere, "Tammerfors," and Suodenniemi).
 P-78 From Kuru, 40 km. north of Tampere, "Tammerfors." Analyzed by N. Sahlbom, reported by Hackman.⁸
 P-77 From west of Kalvolanjärvi, northwest of Hämeenlinna, "Tavastehus."
 P-82 (Unakite, Helsinkite) from Tarvala in Laukaa. Described by Wilkman.⁹

Radium content of Group II.

Coastal

Serial No.	Grams $\times 10^{-12}$ Ra per gram rock
P-75	5.51*
P-76	0.91
P-79	1.55
<i>Interior</i>	
P-80	2.30
P-81	1.55
P-78	3.17
P-77	1.87
P-82	3.28

GROUP III.

The sedimentary rocks of eastern and northern Finland belonging to the Karelidic Cycle are penetrated by the post-Kalevian granites, called "post-Jatulian," which comprise Group III. Only one sample of these granites has been investigated. But Seder-

⁶ Sederholm, J. J.: Granit-gneis problemen i Åbo—Ålands Skärgård, Geol. För. Förh., 46, 1924; The Åland Islands, Bull. comm. géol. Finlande, No. 107, 1934.

⁷ Mäkinen, E.: Ein archaisches Konglomerat von Lavia, Geol. För. Förh., 37, 418, 1915.

⁸ Hackman, V.: Bull. comm. géol. Finlande, No. 15, 1905.

⁹ Wilkman, W.: Über Unakite in Mittel Finnland, Fennia, 50, No. 15, 1928.

* The mica of this sample was separated by a magnet and was found to have a radium content of 13.47×10^{-12} grams of radium per gram of mica.

Radium Content of pre-Cambrian Granites of Finland. 229

holm has paralleled certain granites in Sweden and Norway (Nos. 93 and 94) with the post-Jatulian granites in Finland.

Serial No.

P-86 From Ounasjoki in Rovaniemi, end of the railway in northern Finland.⁸

P-93 From Tranås, Småland, Sweden.

P-94 From Kristiansand, Norway.

Radium content of Group III.

Serial No.	Grams $\times 10^{-12}$ Ra per gram rock
P-86	0.43
P-93	3.144
P-94	0.566

GROUP IV.

Rapakivi granites and other late pre-Cambrian granites.*

Serial No.

P-83 From Åva, north of Brändö, Åland Archipelago.²

P-84 From Onas, 30 km. east of Helsingfors.¹⁰

P-85 From Obbnäs, 40 km. west of Helsingfors.⁴

P-87 From Rödglaskär, north of Enklinge, Åland Archipelago.^{11, 2, 8}

P-88 From Storskär, Gustaf Sökn, Åbo Archipelago.¹²

P-89 From Pula, center of the Viborg area, a "true rapakivi."

P-90 From Viborg, eastern end of Viborg area, a "true rapakivi."

P-91 From south of Bockholm and east of Pellinge, western end of the Viborg area.

P-92 From Salmi, the Ladoga area.

Radium content of Group IV.

Serial No.	Grams $\times 10^{-12}$ Ra per gram rock
P-83	1.21
P-84	1.03
P-85	1.48
P-87	2.21
P-88	1.13
P-89	1.60
P-90	2.74
P-91	1.47
P-92	0.92

In the following paper Dr. Barth discusses these samples and the relations existing among the rocks which they represent.

¹⁰ Borgström, L.: Das Granitgebiet von Onas. Helsingfors, 1931.

¹¹ Sederholm, J. J.: Granit-gneiss problemen i Åbo-Ålands Skärgård, Geol. Förh., 46, 1924.

¹² Kanerva, I.: Über das Rapakivigebiet von Vehmaa in südwestlichen Finnland, Fennia, 50, No. 40, 1928.

* The granites Nos. 83, 84, and 85 are not of the rapakivi type, but like the rapakivis they are younger than the youngest mountain folding in southern Finland. Sederholm tentatively regarded them as contemporaneous with the granites of group III in northern Finland.

RADIUM AND THE PETROLOGY OF CERTAIN GRANITES OF FINLAND.

TOM. F. W. BARTH.

ABSTRACT.

The radium content of various types of granites of Finland is compared with certain petrologic characteristics of the several rocks. No relation is found between radium and potash or ferrous oxide, but for granites belonging to the same type the radium content can be correlated with the amount of biotite.

GEOLOGY OF THE FINNISH GRANITES.

Finland forms the eastern part of the great Fenno-Scandian shield, which, like the Canadian shield, is preponderantly composed of crystalline rocks of pre-Cambrian age. It is generally believed that various regional mountain foldings took place in pre-Cambrian time and that most pre-Cambrian areas show vestiges of these old mountain chains. In Finland detailed geological mapping has shown the existence of several zones of pre-Cambrian folding, the relative age of which has been worked out by Sederholm and his school, who succeeded in demonstrating several distinct pre-Cambrian cycles of sedimentation defined by their relation to tectonic movements. By referring the various granites of Finland to their respective zones of folding, a chronological classification has been obtained.

Svecofennian Zone in Southwestern Finland.

The rocks of this zone strike about E—W and dip more or less vertically (see map, Fig. 1). The oldest are the leptites—fine-grained, metamorphic rocks of partly volcanic, partly sedimentary origin. The leptite formation is penetrated by the so-called *granites of the first group* frequently exhibiting a quartz dioritic composition with differentiation products of more basic character. The typical mode of occurrence is that of anticlinal batholiths—regular massives anticlinally surrounded by layers of schists and gneisses. These rocks are probably among the oldest granites known in the earth's crust; their geological age may therefore be close to 2,000 million years. They almost always show gneissic structure, and are

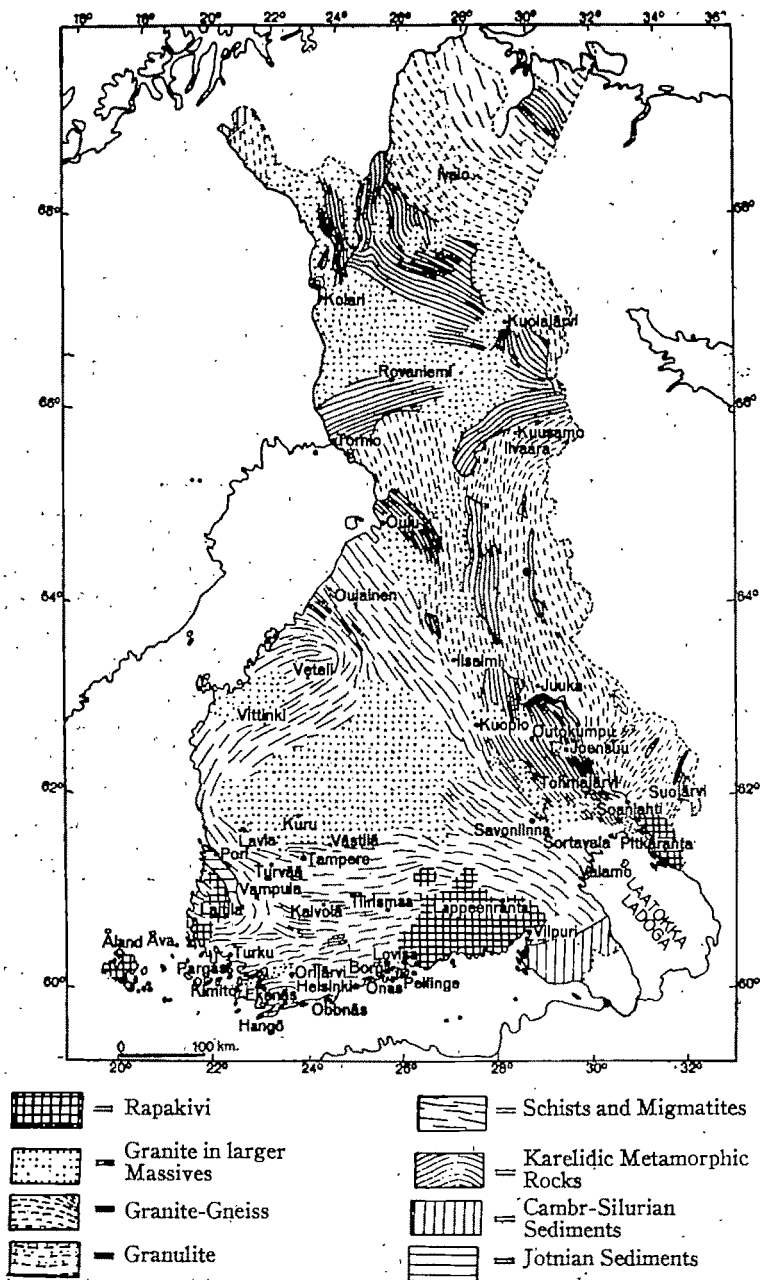


Fig. 1. Rocks of Finland (after Eskola).

often referred to as "gneissose granites." Samples from Åland (No. 71), and from the southern shore of Finland (Nos. 72, 73, and 74) belong to this group.

Younger than the leptites is the Bothnian Formation, comprising a great variety of crystalline rocks of sedimentary as well as eruptive origin, penetrated by the so-called *granites of the second group* which are usually rich in microcline and consequently rich in potash. They evidently intruded the sediments at a time of very active mountain folding. They are typical "serorogenic" granites,¹ intimately connected with migmatization and anatexis. Over great areas they form, with the sediments, injection gneisses and other types of mixed rocks strongly influenced by assimilation and palingenic processes. Several granites of the second group have been sampled: Nos. 75, 76, and 79 from the southern coast of Finland, Nos. 77, 78, 80, 81, and 82 from the interior.

Karelidic Zone in Eastern and Northern Finland.

The rocks of this zone strike northerly and dip more or less vertically. Large areas of post-Karelian granites, the so-called *granites of the third group*, are encountered in northern Finland. But these granites have been sampled from one locality only: Rovaniemi (No. 86).

Rapakivi Granites.

Rapakivi Granites (*granites of the fourth group*) and related basic rocks of southern Finland are younger than any of the pre-Cambrian mountain foldings. Their absolute age has been estimated by Holmes² as 1,000 million years. The rapakivi granites of Finland are famous in petrographic literature; it is hardly necessary, therefore, to devote much space to them here, but references to the newest literature are given, and it should be consulted for further information. Quite recently the question of the genesis of the rapakivi granites has aroused much discussion because of Backlund's propounding a

¹Cf. Wahl, W.: Om granitgrupperna och bergskedjeveckningarna i Sverige och Finland, Geol. Förh., 58, 90, 1936.

²Holmes, A.: On radioactivity and geologic age, abstracted in Compt. Rend. Réunion int. étude du précambrien et des vieilles chaînes des montagnes, edited by Sederholm, Helsinki, 1933.

granitization-theory disclaiming the primary, magmatic character of the rapakivi granites and similar rocks.³

Be this as it may, it is practical to discriminate petrographically between the "true rapakivi" with large ovoids of potash feldspar encompassed by a shell of oligoclase, and the coarse, porphyritic "rapakivi granite" without any shells of oligoclase. Wahl⁴ has named these types "Viborgite" and "Pyterlite" respectively. The rapakivi bodies are very homogeneous, so the chemical analyses quoted in Table IV would seem to be quite representative of the samples collected, although in no case was the sample taken from exactly the same locality as the material analyzed. Characteristic of all rapakivi rocks is idiomorphic quartz; the occurrence of orthoclase as primary potash feldspar that only in part has been inverted to microcline; the reddish-brown pigmentation of the feldspar; the general occurrence of fluorite which can be recognized in almost any hand specimen; the abundance of miarolitic interstices; and finally the absolutely massive structure.

RELATION BETWEEN PETROLOGY AND RADIUM CONTENT.

From measurements on granites of Finland by Poole and Joly,⁵ Holmes⁶ has concluded that potash-rich granites are also rich in radium (uranium). Other authors have concurred. In a recent synopsis, Urry⁷ states that a rough correlation

³ See Backlund, H. G.: Der "Magmaaufstieg" in Faltegebirgen, Bull. comm. géol. Finlande, No. 115, 293-347, 1936 (Compt. rend. soc. géol. Finlande, No. 9); The rapakivi puzzle, Geol. För. Förh., 60, 105-112, 1938; Problems of the rapakivi granites, J. Geol., 46, 339-396, 1938; Zur Granitisationstheorie, Geol. För. Förh., 60, 177-200, 1938. See also Eckermann, H. v.: The genesis of the rapakivi granites, Geol. För. Förh., 59, 503-524, 1937; 60, 113-115, 1938.

⁴ Wahl, W.: Die Gesteine des Wiborger Rapakivigebietes, Fennia, 45, No. 20, 1925.

For a more comprehensive treatise of the geology and petrology of the granites in Finland the reader is referred to the following publications: Eskola, P.: Petrographische Charakteristik der kristallinen Gesteine von Finnland, Fortschr. Mineral. Krist. Petrog., 11, 57-112, 1927; Sederholm, J. J.: Pre-Quaternary rocks of Finland, Bull. comm. géol. Finlande, No. 91, 1-47, 1930; On the geology of Fennoscandia, idem., No. 98, 1-30, 1932.

⁵ Poole, J. H. J., and Joly, J.: The radioactivity of basalts and other rocks, Phil. Mag. (6), 58, 819, 1924.

⁶ Holmes, A. (Contribution to the theory of magmatic cycles, Geol. Mag., 63, 1926, p. 306) gives the following summary of radium in granites of Finland:

	Group I.	Group II, III.	Group IV.
Ra 10^{-13} g./g.	2.36	4.60	6.21
K ₂ O %	2.51	3.61	5.06

⁷ Lane, A. C., Editor: Report of the Committee on the Measurement of Geologic Time, National Research Council, 1936.

between the Ra and the K content of all types of rocks is still found.

In Fig. 2 the radium content of the granites of Finland examined by us has been plotted against their potash content.

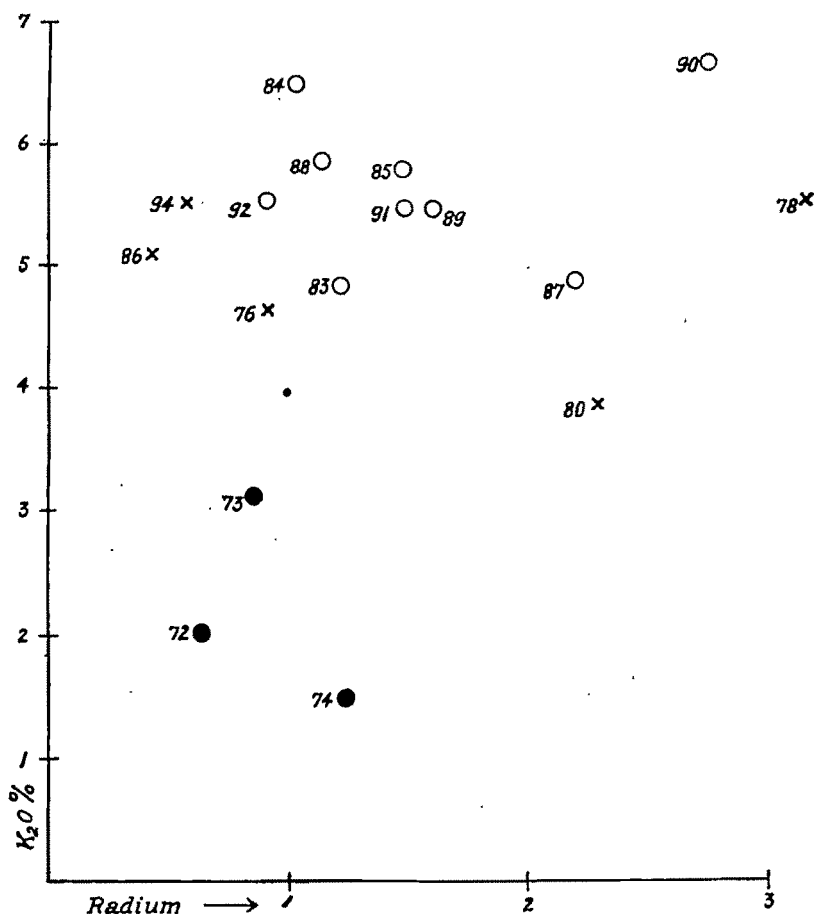


Fig. 2. Content of radium expressed as grams $\times 10^{-12}$ Ra per gram of rock plotted against the percentage of K₂O in the rock. Closed circles = granites of group I, crosses = granites of group II, open circles = granites of group IV.

If any such relation exists in these rocks it is very rough, and more data would be needed to demonstrate it.

Microscopic studies of these granites indicated that biotite-rich granites were also rich in radium. A determination of the biotite content of the Finnish granites was made with the microscope, using the Rosiwal method. At the same time the

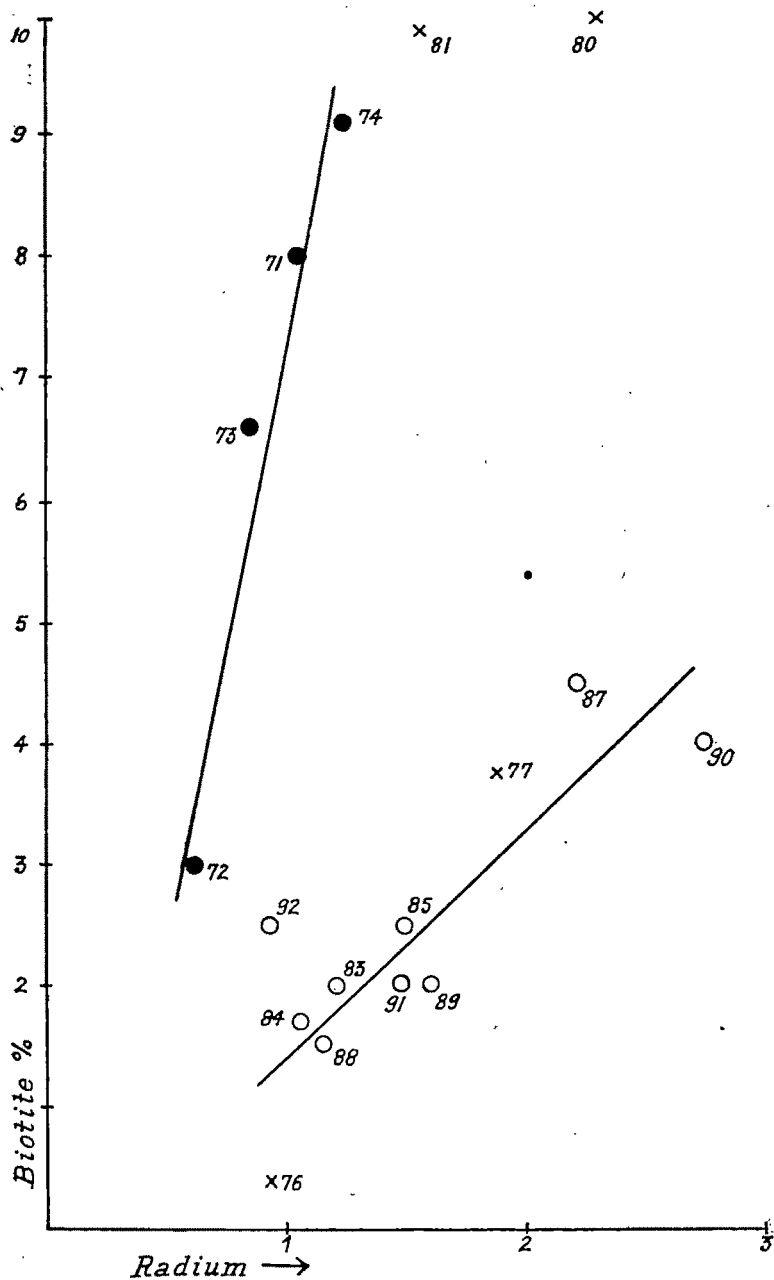


Fig. 3. Content of radium expressed as grams $\times 10^{-12}$ Ra per gram of rock plotted against the volume percentage of biotite in the rock. Symbols as in Fig. 2.

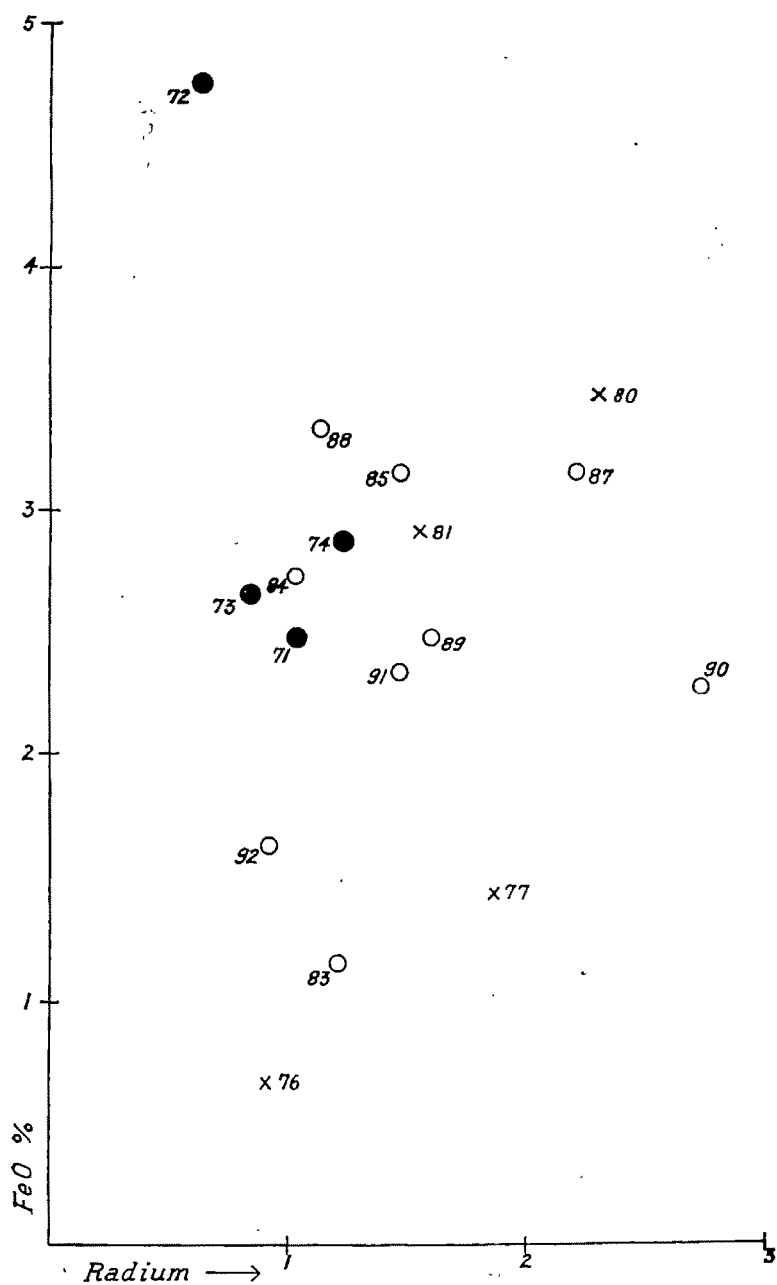


Fig. 4. Content of radium expressed as $\text{grams} \times 10^{-18} \text{ Ra per gram of rock}$ plotted against the percentage of FeO in the rock. Symbols as in Fig. 2.

hornblende content was measured, and as a check ferrous iron was determined by titration in each sample. These data are entered in Tables I to IV and are plotted in the graphs 3 and 4.

Consider the four granites of group I. If the biotite content is plotted against the radium content, the four points lie nearly on a straight line which intersects the horizontal axis not far from the origin. Thus the data on these four rocks would agree with an assumption that most of the radium was in the biotite and that the quantity per gram was nearly the same in each case.

Consider now the nine granites of group IV. If again the biotite content is plotted against the radium content we get similar results; the points lie fairly close to a straight line that passes not far from the origin. Again it appears that there is a tendency for the radium to be concentrated in biotite and for the radium content per gram of biotite to be constant.

Consider finally the eight granites of group II. As stated in a previous section, geologically and petrologically these granites differ from the others. Most of the rocks of group II have been subjected to anatectic processes as well as to contamination from sedimentary material. Some (Nos. 79 and 82) have recrystallized in the *helsinkite* facies (*unakitite* facies) in which biotite is unstable and chlorite and epidote are formed instead. The unusually high radium content of some of these granites (Nos. 75, 78, and 82) is possibly due to some special cause. Excluding rocks of the *helsinkite* facies and rocks with an exceptionally high radium content, only four rocks of the second group are left: Nos. 76, 77, 80, and 81. The data for these are plotted as crosses in Fig. 3. The points are too few and too scattered to locate a line properly, but the best line that can be drawn indicates that here again the quantity of radium per gram is greater in the biotite than in the rest of the rock.

It is interesting to note that in two granites previously examined by Piggot and Merwin⁸ the radium was concentrated in the biotite:

Stone Mountain granite,

3.80×10^{-12} g. radium per g. of rock, and
 11.3×10^{-12} g. radium per g. of biotite.

North Jay granite,

3.4×10^{-12} g. radium per g. of rock, and
 20.7×10^{-12} g. radium per g. of biotite.

⁸ Piggot, C. S., and Merwin, H. E.: Radium in rocks: IV, *This Journal*, 23, 49-56, 1932.

And in rock No. 75 Piggot found (see preceding paper) :

5.51×10^{-12} g. of radium per g. of rock, and
 13.47×10^{-12} g. of radium per g. of biotite.

Unfortunately, the data of the present paper are too scanty to give any quantitative information regarding the more exact location and association of the radium in the granites here considered. "To reason without data," says Tutton, "is nothing but delusion." There is, however, qualitative agreement between Piggot's findings as quoted above and the relation between radium and biotite in the Finnish granites. In each group plotted in Fig. 3 the radium content per gram of biotite, calculated from the straight line, is greater than that of the remainder of the rock. Some of these granites carry hornblende, others do not. If the radium content of the hornblende is higher than that of the salic minerals this is a disturbing factor. If graphs analogous to Fig. 3 are prepared plotting biotite + hornblende against radium the points are very scattered. If, however, we plot biotite + some fraction of the hornblende against the radium content the scattering is decreased, and when the fraction of hornblende used is $\frac{1}{4}$ or less the points lie on straight lines about as well as they do in Fig. 3. In the present granites the content of ferrous iron must be roughly proportional to the content of biotite + hornblende, accordingly a rough relationship might possibly be expected between Ra and FeO. As seen from Fig. 4, however, no such relation is evident.

TABLE I.
Granites of Group I.

Serial No.*	P-71	P-72	P-73	P-74	Average
Ra, 10^{-12} g./g.	1.04	0.63	0.85	1.23	0.94
FeO, weight %	2.47	4.77	2.65	2.88	3.17
Biotite, volume %	8.0	3.0	6.6	9.1	} 9.1
Hornbl., volume %	0.6	9.2	
SiO ₂	70.75	67.36	71.69	...
TiO ₂	0.32	0.61	0.34	...
Al ₂ O ₃	14.54	15.20	13.58	...
Fe ₂ O ₃	0.48	0.85	0.62	...
FeO	2.15	2.80	3.78	...
MnO	0.06	0.10	...
MgO	0.98	1.30	1.16	...
CaO	3.86	3.40	2.23	...
Na ₂ O	3.64	3.93	3.90	...
K ₂ O	2.03	3.12	1.53	...
P ₂ O ₅	0.88	...	0.21	...
H ₂ O	0.53	0.84	0.61	...

* Serial numbers correspond to those used in the preceding paper by Piggot.

P-71. *Granite from Bockholm, Enklings, in the Åland Archipelago.* A description of this locality has been given by Sederholm [Sederholm, J. J.: On migmatites, etc. (Part III), Bull. comm. géol. Finlande, No. 107, 1934]. The granite is here overlain by a conglomerate separating it from the sediments of the second cycle, and this conglomerate contains also pebbles of the same granite, which therefore necessarily must be older.

P-72. *Gneissose granite from Pāvskär, ca. 40 km. W. of Helsingfors.* This locality has been thoroughly investigated by Sederholm [On migmatites, etc. (Part II), Bull. comm. géol. Finlande, No. 77, 1926]. The Pāvskär granite, which is obviously older than granites of the second group by which it is partly penetrated, contains more than 50 per cent feldspar of which the bulk is oligoclase, biotite is present, but the typical colored mineral in this rock is hypersthene, the content of which may attain 10 per cent. A chemical analysis by A. Zilliacus on a sample taken within a few thousand feet of the same locality is entered in Table I.

P-73. *Gneiss-granite from Bergholm, E. of Pelling, 80 km. E. of Helsingfors.* This is a granite of the so-called Vätškär type. The locality has been studied in great detail by Sederholm [On migmatites, etc. (Part I), Bull. comm. géol. Finlande, No. 58, 1923]. As shown by the contact phenomena, the granite of the Vätškär type is obviously older than the granites of the second group. The Vätškär granite is so gneissose that it might properly be designated as a granitic gneiss. The predominant feldspar is oligoclase. Biotite is typical, but hornblende is sometimes present. The chemical composition of this gneissose granite taken from a locality about 2 km. N.N.W. of Bergholm has been determined by E. Mäkinen and is quoted in Table I.

P-74. *Granite from the western shore of Orijärvi.* This granite has been thoroughly investigated by Eskola. [Eskola, P.: Petrology of the Orijärvi Region, Bull. comm. géol. Finlande, No. 40, 1914]. It is an oligoclase granite which in the middle of the Orijärvi batholith contains 36 per cent oligoclase and 1 per cent biotite. Towards the selvages of the batholith the content of both oligoclase and biotite increases. A sample of this contact rock analyzed by Laitakari was taken from the western shore of Orijärvi, but it contains more mica (17.5 per cent) than the rock investigated by us. Laitakari's analysis is quoted.

TABLE II.
Granites of Group II.

Serial No.*	Coast Granites				Central Granites			
	P-75	P-76	P-79	P-80	P-81	P-78	P-77	P-82
Ra, 10 ⁻¹² g./g.	5.51	0.91	1.55	2.30	1.55	3.17	1.87	3.28
FeO, weight %	1.34	0.64	0.50	3.48	2.94	1.34	1.44	2.08
Biotite, volume % ...	4.9	0.4	0.1	10.0	9.9	0.7	3.7	0.1
Hornbl., volume %	3.0	...	1.4
SiO ₂	74.76	...	66.18	...	73.03
TiO ₂	0.02	...	0.48	...	0.20
Al ₂ O ₃	13.37	...	16.25	...	14.41
Fe ₂ O ₃	0.72	...	0.50	...	0.68
FeO	0.86	...	4.35	...	1.25
MnO	tr.
MgO	0.23	...	2.17	...	0.38
CaO	1.11	...	3.46	...	1.41
Na ₂ O	3.65	...	2.80	...	3.03
K ₂ O	4.62	...	3.90	...	5.58
P ₂ O ₅	tr.
H ₂ O	0.50	...	0.35	...	0.39

* Serial numbers correspond to those used by Piggot (see preceding paper).

P-75. *Granite from Kunnlinge, Åland Archipelago*, has been described by Sederholm [On migmatites, etc. (Part III), Bull. comm. géol. Finlande, No. 107, 1934]. It is of certain post-Bothnian age. It penetrates the gneissose granite (No. P-71) and the Bothnian sediments of the same locality.

P-76. *Granite from Ingå, ca. 40 km. W. of Helsingfors*. The region has been thoroughly investigated by Sederholm [On migmatites, etc. (Part II), Bull. comm. géol. Finlande, No. 77, 1926]. The Ingå granite forms a special type characterized by having fewer inclusions than the ordinary coast granite. Microcline predominates, oligoclase is also present; it is poor in colored constituents: biotite and chlorite; a red garnet sometimes occurs. The analysis (by A. Ziliacus) was made on a sample from Svenviken in Ingå.

P-77. *Granite W. of Kalvolanjärvi, N.W. of Hämeenlinna (Tavastehus)*. This rock is from a great post-Bothnian granite massive, the exact geological relations of which have not been worked out in detail. Microcline predominates but oligoclase is not uncommon. Biotite is the only colored mineral. The structure is gneissose.

P-78. *Granite from Kuru, 40 km. N. of Tampere (Tammerfors)*, again belongs to the younger subgroup. This locality is in the center of a large area of equi-granular, medium-grained, grey granites in central Finland. A sample from this exact locality has been analyzed by N. Sahlbom. The rock is a typical microcline granite with a small amount of oligoclase-albite; both biotite and hornblende occur as colored constituents. The reason for the very high radium content of this rock is not known. It is probably due to the presence of some radioactive mineral (nothing, however, could be detected in the thin sections), so the normal relation between radium and biotite does not hold in this rock.

P-79. *Granite (Helsinkiite)* from Kajholmen, ca. 20 km. E. of Helsingfors, is a typical coast granite of the so-called Hangö type. It is always full of inclusions and is quite likely a palingenic granite originated by anatexis of older gneisses. Microcline is the typical feldspar. The original oligoclase is usually broken up in an aggregate of sericite and albite. Biotite seems not to be stable, chlorite and serpentine having crystallized instead. Along shear zones a red epidote is plentiful. It is obvious that the relation between radium and biotite does not hold since the biotite is unstable in this granite. The age is also uncertain in so far as the replacement processes may be younger than the granite.

P-80. *Granite from Lavia* belongs to the younger subgroup of the post-Bothnian granites. It has been studied and analyzed by Mäkinen [Mäkinen, E.: Ein archaisches Konglomerat von Lavia, Geol. För. Förh., 37, 418, 1915] and by him called granodiorite (the analyzed specimen, however, was taken west of Välimäki, several miles west of the locality of our sample). Andesine is the typical feldspar, microcline being rather unimportant; both biotite and hornblende are usually abundant.

P-81. *Granite from Siuro* (on the highway between Tampere [Tammerfors] and Suodenniemi) belongs to the oldest subgroup of the post-Bothnian granites. This locality has not been specially studied but neighboring areas have been intensively examined by Sederholm and Mikkola [Sederholm: On the sub-Bothnian unconformity, etc., Bull. comm. géol. Finlande, No. 95, 1931]. The typical feldspar is andesine, microcline is unimportant, biotite is the only colored constituent. The structure is gneissose. Mineralogically the granite closely resembles its younger congener, No. 80.

P-82. *Granite (Unakite, Helsinkiite)* from Torvala in Laukaa. This is a typical post-Bothnian unakite (or helsinkiite) from central Finland as described by Wilkman [Wilkman, W. W.: Über Unakite in Mittel Finnland, Fennia, 50, No. 15, 1928]. It is characterized by the mineral association albite and epidote (both plagioclase and biotite being unstable). Strictly speaking, it is not a granite, and thus does not fall within the scope of the present paper. For a more comprehensive petrographic description and chemical analysis the paper of Wilkman should be consulted.

TABLE III.
Granites of Group IV.

Serial No.*	P-83†	P-84	P-85	P-87	P-88	P-89	P-90	P-91	P-92	Average
Ra, 10 ⁻¹² g./g.	1.21	1.03	1.48	2.21	1.13	1.60	2.74	1.47	0.92	1.53
FeO, weight % ...	1.16	2.72	3.15	3.16	3.32	2.47	2.29	2.33	1.62	2.47
Biotite, volume %	2.0	1.7	2.5	4-5	1-2	2	4	2	2-3	5.2
Hornbl., volume %	2.0	4.2	5-6	6-7	3	3	
SiO ₂	72.63	73.78	68.40	70.56	71.43	70.24	71.53	75.81	75.26
TiO ₂	0.29	0.24	0.52	0.44	0.83	0.35	0.32	0.25
Al ₂ O ₃	13.33	11.52	14.57	12.27	12.29	14.28	13.70	11.22	12.71
Fe ₂ O ₃	0.72	1.35	0.87	2.74	1.09	0.63	1.79	0.86	0.97
FeO	1.72	2.37	3.57	2.93	3.33	2.88	2.35	1.91	1.11
MnO	0.04	0.06	0.14	0.06	0.04	tr.	0.02
MgO	0.63	tr.	0.72	0.65	0.22	• 0.22	0.48	0.34	0.29
CaO	1.88	0.92	2.84	1.87	2.10	2.09	2.08	1.25	0.66
Na ₂ O	3.07	2.50	2.21	3.20	2.38	3.16	2.82	2.27	2.65
K ₂ O	4.82	6.49	5.79	4.92	5.87	5.50	6.71	5.49	5.56
P ₂ O ₅	0.19	0.05	0.25	0.13	0.08	0.04
H ₂ O	0.12	0.66	0.68	0.60	0.66	0.41	0.34	0.40	0.89

* Serial numbers correspond to those used by Piggot, see preceding paper.

† The analysis of this granite shows also the following additional constituents:
S = 0.11, SrO = 0.00, BaO = 0.08, Cl = 0.09, CO₂ = 0.21.

P-83. *Granite from Ava*, N. of Brändö, Åland Archipelago [Sederholm: On migmatites, etc. (Part III), Bull. comm. géol. Finlande, No. 107, 1934], forms an isolated body which is certainly younger than the granites of the second group. Some of it is fine-grained, but coarse types are also found. Quartz usually has a bluish tinge. Microcline is by far the dominant feldspar, only a very small amount of oligoclase being present. Biotite represents the only colored constituent.

P-84. *Granite from Onas*, 30 km. E. of Helsingfors, has been described by Borgström [Borgström, L.: Das Granitgebiet von Onas. Helsingfors 1931 (Centraltryckeriet)]. According to two chemical analyses it resembles chemically the rapakivi granite type. An analysis by Sandelin is quoted in Table III. This granite forms a homogeneous, transgressive body measuring about 270 km.² It is obviously the youngest formation in this area and may be contemporaneous with the rapakivi granites (of the fourth group). Microcline is the typical feldspar. Both biotite and hornblende occur as colored constituents. Fluorite and zircon are accessories. The granite is homogeneous and coarse-grained.

P-85. *Granite from Obbnäs*, 40 km. W. of Helsingfors, has been studied by Sederholm [On migmatites, etc. (Part II), Bull. comm. géol. Finlande, No. 77, 1926]. It constitutes a coarse-grained aggregate of red microcline, greyish white oligoclase, dark grey quartz, and black biotite and hornblende. Titanite, apatite, zircon, and fluorite are accessories. A chemical analysis by Eskola is quoted in Table III. Geologically the granite forms a structureless body, about 250 km.² in surface area, which pierces through all the other rocks of this region.

P-87. *Rapakivi from Rödglasskär*, N. of Enklinge, Åland Archipelago, is characterized by small ovoids of oligoclase (usually 1 to 2 cm. in diameter). The locality has been described by Sederholm [On migmatites, etc. (Part III), Bull. comm. géol. Finlande, No. 107, 1934]. Chemical analysis by Sahlbom.

P-88. *Rapakivi* from Storskär, Gustaf Sökn, Åbo-Archipelago. A good description and detailed map of the rapakivi area of which this sample is a representative have been published by Kanerva [Kanerva, I.: Rapakivigebiet von Vehmaa, Fennia, 50, No. 40, 1928]. The chemical analysis was made by E. A. O. Nordensvan and has been quoted from the paper by Kanerva.

P-89. *Rapakivi Granite*, Palsa, center of the Viborg area. It is a "true rapakivi," as is also

P-90. *Rapakivi* from Viborg (eastern end of the Viborg area) with ovoids of potash feldspar encompassed by a shell of oligoclase.

P-91. *Rapakivi* S. of Bockholm, E. of Pelling (western end of the Viborg area) has no oligoclase ovoids and should thus be called pyterlite. The three last-mentioned granites (Nos. 89, 90, and 91) are all from the so-called Viborg Rapakivi Area, 20,000 km.² in extent, and thus the largest of the rapakivi occurrences. For detailed petrographical and chemical information the reader should consult a paper by Wahl [Wahl, W.: Die Gesteine des Wiborger Rapakivigebietes, Fennia, 45, No. 20, 1925], from which analyses 89, 90, and 91 are all taken.

P-92. *Rapakivi Granite* from Salmi, Ladoga area, is a pyterlite without shells of oligoclase around the potash feldspar. The analysis (by G. Sundell) was made on a sample from the Pitkäranta mine.

TABLE IV.
Other Granites from Fennoscandia.

Serial No.	P-86	P-93	P-94
Ra, 10^{-12} g./g.	0.43	3.14	0.57
FeO, weight %	0.85	...	2.11
Biotite, volume %	1.1	0.2	4.2
Hornbl., volume %	1.0	...

The granites of the third group in northern Finland and Sweden, i.e. the Lapland granites (No. 86), have been paralleled by Sederholm with the Småland granites of middle Sweden (No. 93) and the Telemark granites of Norway (No. 94). Results of studies of representative samples of these granites have been entered in the above table. The analyzed sample of the Småland granite seems to have an abnormally high radium content. The other samples, if representative, seem to correspond most closely to the granites of the first group in Finland.

CONCLUSIONS.

As far as the present data go they indicate that radium is associated more with the biotite of Finnish granites than with the other mineral components and that in each group (Fig. 3) the total amount of radium increases with the biotite content. No correlation is found between Ra and FeO or between Ra and K_2O . It seems rational, therefore, to correlate radium with the mineralogy rather than with the chemistry of a granite. Granites of group I contain less radium than do granites of group IV (both total radium and radium per gram of biotite). But more data are required to show whether this is fortuitous or conditioned by such factors as geologic age (which must have some influence), mineral composition, or, as Backlund thinks, special mode of origin (granitization of sediments).

ACKNOWLEDGMENT.

The writer is greatly indebted to several Finnish geologists through whose coöperation this investigation was made possible. Grateful acknowledgment of the generous help of the following is hereby made: Dr. J. J. Sederholm, the late director of the Geological Survey in Finland, who took great interest in this work and spent a considerable part of the summer of 1932 in the field with the author; Drs. L. Borgström and

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THE SYSTEM, $\text{CaSO}_4\text{—H}_2\text{O}$.

E. POSNJAK

ABSTRACT.

Since the appearance many years ago of the investigation by van't Hoff and his associates on the various calcium sulphates and their relationships, which formed part of their classical work on the formation of the Stassfurt salt deposits, there has been an unending controversy regarding the true state of affairs in the system, $\text{CaSO}_4\text{—H}_2\text{O}$. No attempt, however, is made to give a detailed review of this literature. After considering the facts which have been brought out, and checking experimentally some that seemed most pertinent, the present investigation found that the basis for most disagreements was some erroneous suppositions regarding phase relations involving hydrated compounds. These misled van't Hoff et al. to assume that a dissociation reaction took place when they found that under certain conditions anhydrite, and, as they thought, "soluble anhydrite" also, had crystallized in solutions at the expense of gypsum. As a result of this, and the sluggishness of reaction in the case of the formation of hemihydrate, their data are erroneous.

Data brought out by various investigators, which are recounted in the text, furnish definite and reliable information regarding the system, $\text{CaSO}_4\text{—H}_2\text{O}$, between 0 and 200°. The transition point, gypsum—anhydrite, lies at $42 \pm 1^\circ$, and that of gypsum—hemihydrate at $97 \pm 1^\circ$. In the region between these two temperatures, gypsum is truly metastable. The transition point for hemihydrate into "soluble anhydrite" ($\gamma\text{-CaSO}_4$) lies apparently at a high temperature, and, owing to the instability of the two phases, cannot be established. A monotropic relation exists between anhydrite ($\beta\text{-CaSO}_4$) and "soluble anhydrite" ($\gamma\text{-CaSO}_4$).

Regarding the geologically important question of the conditions under which anhydrite may be deposited at ordinary temperatures, available information indicates that a high concentration of salt solutions is not required, but that anhydrite may be deposited from relatively dilute solutions.

INTRODUCTION.

The very extensive, though contradictory, literature which has grown around the hydrated and anhydrous calcium sulphates shows the importance and interest these compounds present, both technologically and scientifically. The most comprehensive investigation of the phases and their relationship in the system, $\text{CaSO}_4\text{—H}_2\text{O}$, was carried out almost forty years ago by van't Hoff and his associates¹ in connection with their classical work on the conditions of formation of the Stassfurt salt deposits. But despite the apparently incontrovertible evidence on which their conclusions seemingly were based, hardly a year has passed since then without the appearance of

¹ van't Hoff, J. H., Armstrong, E. F., Hinrichsen, W., Weigert, F., and Just, G.: *Z. phys. Chem.*, 45, 257, 1903; also van't Hoff, J. H.: *Bildungsverhältnisse d. ozeanischen Salzablagerungen*, Leipzig, 1912.

some paper which questioned the correctness or accuracy of one or another particular point of their investigation. More recently, Ramsdell, Partridge, and White² have reviewed and re-examined the more important questions that have been raised by various investigators, and concluded that it was necessary to modify very significantly the interpretation given by van't Hoff of the relations that exist in the system, $\text{CaSO}_4\text{—H}_2\text{O}$. They denied the individual existence of one of the solid phases ("soluble anhydrite"), and they also found important differences in values given for the transition temperatures. However, the evidence regarding the character of "soluble anhydrite" was not convincing, and besides they failed to offer any satisfactory explanation for the apparently necessary rejection of van't Hoff's experimental proofs. In view of this the controversial character was in no way removed from the interpretation of this system.

It seemed very surprising that, considering the relative simplicity of the system, $\text{CaSO}_4\text{—H}_2\text{O}$, and its accessibility for study, it could remain over a period of so many years the subject of so much controversy. Definite knowledge of the relations of the different phases appearing in this system is not only technologically important, but is also of much geological interest since in most sedimentary processes calcium and sulphate ions are present, and therefore deposition of calcium sulphate in some form is of very common occurrence. In view of this it seemed very desirable to undertake some further experiments in the hope of gaining a better understanding of this system. These experiments, carried out over seven years ago, again yielded results that could not be reconciled with van't Hoff's experimental evidence and interpretation, but as no explanation of this could at that time be found, publication did not seem warranted. The appearance recently of an article by Weiser, Milligan, and Ekholm³ proving the individual existence of "soluble anhydrite," and another by Hill⁴ on the transition point, gypsum—anhydrite, both confirming the author's results, would have made it superfluous to publish them now. But general considerations of phase relations involving hydrated compounds have led the author to conclusions which throw much light on the phase relations that exist

² Ramsdell, L. S., and Partridge, E. P.: *Am. Mineral.*, 14, 59, 1929; Partridge, E. P., and White, A. F.: *J. Am. Chem. Soc.*, 51, 360, 1929.

³ Weiser, H. B., Milligan, W. O., and Ekholm, W. C.: *J. Am. Chem. Soc.*, 58, 1261, 1936.

⁴ Hill, A. E.: *J. Am. Chem. Soc.*, 59, 2242, 1937.

in the system, $\text{CaSO}_4\text{—H}_2\text{O}$, and which show at once that much of the experimental evidence given by van't Hoff, which seemed so well founded theoretically, is in reality untenable and based on misapprehensions. In view of this, a restatement of the more important facts pertaining to the phases that enter into this system, and their relations, now seems to be justified, as it promises to bring to an end the uncertainties and controversies that have surrounded this system for so long a time.

THE SOLID PHASES.

Van't Hoff and his coworkers⁵ had accepted the existence of the following four solid phases: anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), and "soluble anhydrite" (CaSO_4). It is the last compound that almost from the beginning has provoked much discussion, and a number of investigators came to the conclusion that van't Hoff's "soluble anhydrite" was not a distinct and separate compound, but represented a more or less dehydrated hemihydrate. This led to the idea that the latter was "zeolitic" in its character. Ramsdell and Partridge⁶ reviewed this controversial literature, and on the basis of their own experimental evidence concluded that "soluble anhydrite" does not represent a separate phase, but is "identical in its crystal structure with hemihydrate which belongs to the zeolitic class of substances that lose and regain water of hydration without change in crystal structure." The most recent re-investigation of this subject by Weiser, Milligan, and Ekholm,⁷ however, showed conclusively that hemihydrate and "soluble anhydrite" do not have identical structures and that hemihydrate "behaves in all essential respects like a true chemical hydrate." The same conclusion was reached by the author prior to the publication of the article by Weiser et al., and as many investigations have been published disproving the individual existence of "soluble anhydrite," it is probably appropriate to present this independent evidence.

For the starting point in the investigation of this problem, the observation made long ago by Le Chatelier⁸ was used, that heating curves taken on gypsum showed two distinct breaks:

⁵ Op. cit.

⁶ Op. cit.

⁷ Op. cit.

⁸ Le Chatelier, H.: *Recherches expérimentales sur la constitution des mortiers hydroliques*, Paris, 1887.

the first and larger one at about 128° , and a smaller break at about 163° . Le Chatelier, who was apparently the first to recognize plaster of Paris as calcium sulphate hemihydrate in composition, and its setting as a hydration process in which gypsum is formed, proved that the first break was caused by the formation of the hemihydrate, and ascribed the smaller second break to the heat effect caused by dehydration of the

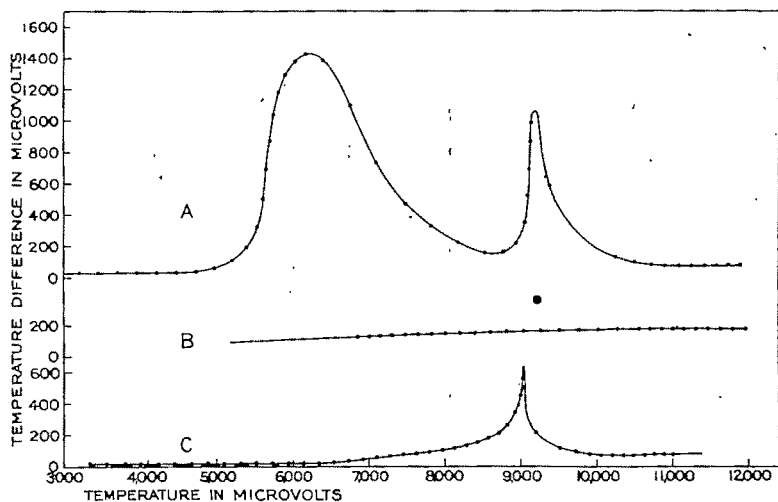


Fig. 1. Differential heating and cooling curves with a copper-constantan thermocouple.

hemihydrate. Van't Hoff stated that they were unable to verify the existence of this second heat effect, which is perhaps not surprising, considering the low sensitivity of the method when an ordinary thermometer is used, as was the case; he and his coworkers had found that anhydrous calcium sulphate was formed below the temperature at which hemihydrate formed, and for this reason attributed to retardation the effect found by Le Chatelier. It was probably this inability of van't Hoff and his associates to duplicate the observation of Le Chatelier that led them to erroneous conclusions throughout their investigation. With thermocouples that are available at present it is easy, however, to verify the correctness of Le Chatelier's observation. In Fig. 1 is shown a typical differential heating curve, A, taken on gypsum (selenite) with a copper-constantan thermocouple. It does not matter, however, what kind of gypsum is used, the same type of curve showing

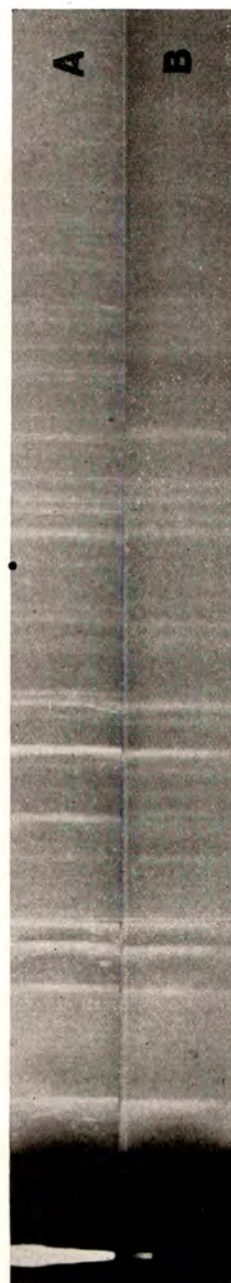


Fig. 2. X-ray diffraction: A hemihydrate, B γ -CaSO₄ ("soluble anhydrite").

two distinct absorptions of heat is always obtained, though the actual temperature of these maxima is of course considerably affected by the rate of heating, and the coarseness of the material. Below the heating curve A is shown a differential cooling curve, marked B, which was obtained on the same material right after the heating curve had been taken, and which shows no heat effects at all. The lowest curve, C, is again a heating curve on the same material after it had stood over night exposed to the atmosphere, and here a decided heat effect corresponding to the one at the higher temperature in curve A is again obtained. These curves thus give ready proof of the correctness of Le Chatelier's work, and substantiate also the criticism of van't Hoff's work by Davis,⁹ who called particular attention to the extremely rapid rehydration of the completely dehydrated gypsum when exposed to the atmosphere. The rapid rehydration explains why several investigators who did not take the necessary precautions to prevent absorption of water, and its recombination to form hemihydrate, came to conclude that the latter and "soluble anhydrite" were structurally one compound of variable composition, similar, as they thought, in behavior to zeolites. When, however, precautions are taken, important structural differences in the two substances are readily found. In Fig. 2 are shown the X-ray diffraction patterns of the two substances, taken with K_{α} -radiation of molybdenum, side by side on the same film, and in Table I are given the measurements of their spacings. The "soluble anhydrite" sample in this case, after being placed in the glass capillary which was open at one end, was kept for a few hours in a furnace at about 200° , and while still hot was quickly sealed off. The data given bring out clearly the differences in the crystal structures of hemihydrate and "soluble anhydrite" and confirm in all essentials the work of Weiser and his coworkers.

Van't Hoff's statement in regard to the existence of four solid phases is therefore correct. The name "soluble anhydrite" which he introduced is a misnomer, however. Not only are there no data in existence regarding its solubility, but, as will be seen farther on, van't Hoff's notion about its solubility arose from mistaking the formation of hemihydrate in his experiments for "soluble anhydrite." As there is definite evidence¹⁰ for the existence of a third modification of anhydrous

⁹ Davis, W. A.: J. Soc. Chem. Ind., 26, 727, 1907.

¹⁰ Grahmann, W.: Neues Jahrb. Mineral. Geol., I, 210, 1914.

calcium sulphate at high temperatures—an enantiotropic inversion of anhydrite to this form is reported to take place at 1195° —it is probably desirable, for the sake of avoiding confusion, to use for the three modifications of calcium sulphate the commonly followed way of distinguishing the different

TABLE I.
X-Ray Diffraction.

Hemihydrate		$\gamma\text{-CaSO}_4$ ("soluble anhydrite")	
Spacing	Intensity	Spacing	Intensity
5.95	8	6.05	10
3.45	7	3.48	6
2.99	10	3.01	9
2.80	10	2.80	9
2.70	1	2.70	1
2.33	1+	2.33	2
2.26	0.5	2.17	1—
2.13	5	2.14	0.5
2.07	0.5—	2.09	1+
2.000	0.5	2.001	1
1.905	1	1.910	2
1.841	9	1.845	6
1.790	0.5—
1.723	2	1.738	2
1.685	4	1.690	4
1.655	3
1.605	0.5
1.526	1	1.540	0.5—
.....	1.505	0.5
1.470	1	1.475	2
1.440	1	1.435	1
1.395	0.5—	1.390	0.5—
1.351	1	1.350	0.5—
1.300	4	1.297	3
1.258	3	1.264	2
1.238	2	1.237	2
1.203	2	1.211	2—
1.165	1	1.160	0.5
1.148	3	1.140	3
1.117	1
1.089	0.5	1.085	0.5
1.074	1
1.064	2
1.055	1	1.049	0.5—
1.036	1+	1.037	1
.....	1.022	0.5
1.009	1	1.003	1
0.995	1—	0.992	1
0.953	0.5	0.951	0.5
0.938	0.5—
0.918	1	0.920	0.5
0.890	1	0.895	0.5

polymorphic modifications: α -CaSO₄ for the high-temperature form, β -CaSO₄ for anhydrite, and γ -CaSO₄ for the "soluble anhydrite."

THE EQUILIBRIUM RELATIONS IN THE SYSTEM, CaSO₄-H₂O,
AS DETERMINED BY VAN'T HOFF AND HIS ASSOCIATES

Establishment of the equilibrium relations between the four solid phases by van't Hoff and his coworkers rested on their determination of three dissociation pressure curves for gypsum: (1) gypsum—hemihydrate, (2) gypsum—"soluble anhydrite" (γ -CaSO₄), and (3) gypsum—anhydrite (β -CaSO₄). On the basis of these dissociation pressure curves they gave the temperature for the transition, gypsum—hemihydrate, at 107°, for gypsum— γ -calcium sulphate at 89-93°, and for gypsum— β -calcium sulphate at 63-66°. The dissociation pressures were not determined directly, however, as according to their statement, the sluggishness of the reaction in every case made it impossible to use the direct method, and for this reason they resorted to indirect ways of evaluating the dissociation pressures. For this purpose, some suitable salt solutions were utilized, which, without interacting with the solids, promoted the desired reaction presumably by increasing their solubility. Since the reaction consisted either in liberation of water, or the reverse—the taking up of water—a suitable method for observing this effect in each case was used, and the equilibrium temperature in the particular salt solution was determined. The dissociation pressure it was assumed would be equal to the vapor pressure of the solution for this temperature, and by determining the latter directly, the desired value for the dissociation pressure was obtained. By applying a thermodynamic formula it was then a simple matter to calculate from two determinations the dissociation pressure over the whole range of temperatures.

This procedure is sound, provided that a dissociation pressure actually exists, and that equilibria are definitely established, which of course van't Hoff and his associates thought they had proved to be the case. However, as will be shown farther on, they were mistaken in this, and as a result, their determinations are erroneous.

It has been mentioned above that van't Hoff and his

coworkers did not succeed in verifying Le Chatelier's experiments showing that the dehydration of gypsum proceeds always in two steps, first forming hemihydrate, which only at a higher temperature loses its water to form γ -calcium sulphate. They stated that neither by observing the temperature on heating gypsum, nor by the dilatometric method, could they find the second discontinuous change. The transition point, gypsum—hemihydrate, according to their determination was at 107° , and though in general, they said, dehydration proceeds stepwise with increasing temperature, and it would be natural, therefore, to expect further dehydration to take place at a higher temperature, certain experiments showed that gypsum changed to anhydrite below this temperature. For this reason they concluded that the upper heat effect of Le Chatelier's curve could have resulted only from delayed transformation, and further, since anhydrite was formed at lower temperature than hemihydrate when in contact with salt solutions of the same concentration, they also concluded that the dissociation pressure had a higher value. That the dissociation pressure existed was taken for granted, and neither they nor apparently any of the later investigators had given attention to the fact that it was only when a commercial plaster of Paris (or gypsum made from it) was used, that anhydrite was formed under these conditions; and that when pure gypsum was used anhydrite was not obtained. Van't Hoff et al.¹¹ said: "Wesentlich ist für das Gelingen dieses Versuches allerdings, dass nicht gewöhnlicher, z.B. präzipitierter Gips genommen wird, denn dieser zeigt auch nach mehreren Wochen nur die Halbhydratbildung. Am einfachsten gelingt derselbe, falls das Dilatometer mit Stuckgips . . . beschickt wird." In view of this it would have been pertinent to inquire why pure gypsum had not changed to anhydrite, although gypsum made from a commercial plaster (Stuckgips) was, as they concluded, dissociating directly to anhydrite. However, no attempt to find the reason for this important fact, or to give any explanation of it, was made, and, as it apparently fitted their notion of dissociation pressures, they used the behavior of this particular plaster in salt solutions to establish the dissociation of gypsum to anhydrite, and also to soluble anhydrite.

¹¹ *Op. cit.*, p. 275.

We see, then, that the whole work of van't Hoff and his coworkers rests on the supposition (1) that gypsum can dissociate in three independent ways, each resulting in a definite dissociation pressure, and (2) that at the temperature at which the change from one solid to the other takes place in the presence of salt solutions a dissociation pressure equal to the vapor pressure of the solution must always exist. That these assumptions are not justified, except for the transition of gypsum to hemihydrate, and that even here their experiments resulted in an erroneously high temperature, will be shown farther on.

BEHAVIOR OF THE VARIOUS CALCIUM SULPHATES IN
RESPECT TO TEMPERATURE.

Gypsum, when exposed to the air at ordinary temperature, is usually stable because the partial water vapor pressure of the atmosphere is greater than its dissociation pressure. If heated to a temperature at which the dissociation pressure of gypsum becomes greater than the surrounding water vapor pressure, it begins to dehydrate. This behavior is utilized in the manufacture of plaster of Paris, that is, of the hemihydrate, from gypsum. The long experience in the manufacture of plaster of Paris presents a consistent record that whenever gypsum is heated at not too high a temperature—usually to about 130°—the product formed is invariably the hemihydrate; and further, that if the temperature is permitted to go considerably higher, the product becomes “dead burned,” it has then been converted into anhydrite. All the records of laboratory experience show that gypsum on dehydration is invariably first converted into hemihydrate, and only after this is dehydrated further to anhydrous calcium sulphate. It is clear from the discussion given earlier that this second step in dehydration results in the formation of γ -calcium sulphate, and that this is a reversible reaction. In fact, its reversibility under ordinary conditions is so rapid, owing to the low dissociation pressure of hemihydrate— γ -calcium sulphate at ordinary temperature, that some investigators have denied the existence of γ -calcium sulphate as a definite compound. With the evidence presented by Weiser et al.,¹² and confirmed in the

¹² Op. cit.

present paper, its individual existence is now well established.¹³ However, the transition point, hemihydrate— γ -calcium sulphate, has not been determined, and it is not likely that it can be determined. We know that the solubility of hemihydrate decreases very rapidly with temperature so that the dissociation pressure at the transition point practically must equal the vapor pressure of water. It would present very considerable experimental difficulties to determine this point directly, either by temperature measurements or from solubility data. But besides, as we shall see below, inversion to β -calcium sulphate takes place at these temperatures at a rate that would probably make it impossible to carry out these experiments. Therefore, all that can be said definitely about this transition is that it takes place at a temperature considerably above the transition point, gypsum—hemihydrate.

The next question of interest is the relation of β - to γ -calcium sulphate. Differential heating curves taken about 100° beyond the heat effect showing the formation of γ -calcium sulphate failed to indicate any further heat effect. The formation of β -calcium sulphate at higher temperatures is of course a well established fact ("dead burned" plaster). Therefore a few experiments were made of heating gypsum at various temperatures, and X-raying the resulting material. After a short heating at 450° , it was found to consist entirely of β -calcium sulphate. When heated at about 300° for 20 hours, the material was mostly β -calcium sulphate. After heating two days at about 250° , an appreciable amount of β -calcium sulphate besides hemihydrate was found. Even below 200° , on prolonged heating, formation of β -calcium sulphate could be

¹³ There exists, however, considerable confusion in the literature dealing with the calcium sulphates in regard to transition points and decomposition, and a few words may therefore be necessary. One meets statements to the effect that at the temperature at which gypsum is decomposed when heated in the air its dissociation pressure is equal to the atmospheric pressure; or, that because the decomposition temperature of hemihydrate found by Le Chatelier was not affected by carrying out this dehydration under reduced pressure, it was not a dissociation pressure. Such confusion may have arisen from the use of the term "boiling gypsum" ("Gipskochen") in the manufacture of plaster of Paris. Dissociation takes place whenever the dissociation pressure becomes greater than the partial water vapor pressure of the atmosphere, and reducing the total pressure has very little effect, as it is in no way similar to a boiling point. The actual temperature at which decomposition is observed on a heating curve depends much on the rate of the dissociation reaction. Unless this rate is rapid, and the experiment is carried out in a closed vessel in which the dissociation pressure would prevail, no information regarding the transition point can be obtained from a heating curve.

detected. The gradual increase in the rate of formation of β -calcium sulphate with increasing temperature, and the failure to observe any discontinuity for the heating curve on γ -calcium sulphate at a temperature where β -calcium sulphate was found to form, indicate that the relation of these two forms of calcium sulphate must be monotropic.

THE CALCIUM SULPHATES AND PHASE RELATIONS.

Gypsum, like other substances containing so-called water of crystallization, loses its water when kept in an atmosphere of sufficiently low water vapor pressure. This takes place at any temperature, but the rate of loss increases with temperature because of the rapid rise of the dissociation pressure of the hydrate. When the surrounding water vapor pressure equals the dissociation pressure of the hydrate, the latter does not lose any of its water. This whole behavior represents a reversible reaction in which, under definite conditions, exists a state of equilibrium between the hydrate on one side, and on the other the water vapor plus the substance formed when the hydrate loses this water. From the point of view of the phase rule this, or any other dissociation equilibrium, represents a two-component univariant system, that is, a three-phase system with one degree of freedom. For each temperature the two solid phases are in equilibrium with a definite vapor phase, and this vapor is the dissociation pressure. If one of the solid phases disappears, the pressure becomes changeable, as we then have a system with two degrees of freedom, and the hydrate can be in equilibrium with various pressures at a given temperature. These, however, are not dissociation pressures, but represent a range of vapor pressures within which the hydrate has a field of stability. The well-established facts in regard to all dissociation pressures show that for the existence of any dissociation pressure there must be a reversible reaction representing a univariant two-component system in which one component is volatile.

If we consider now the three dissociation pressure curves for gypsum, of van't Hoff et al., it becomes obvious from the facts mentioned above concerning the thermal behavior of gypsum that only in the case of the dissociation of gypsum to hemihydrate can the requirement of a reversible reaction that represents a univariant two-component system be met. Neither β - nor γ -calcium sulphate can form directly by removal

of water vapor from gypsum, since in the formation of β -calcium sulphate the intermediate compounds, hemihydrate and γ -calcium sulphate, intervene, and in the case of γ -calcium sulphate the formation of hemihydrate intervenes. In the presence of these intermediate compounds, the two reactions required for the dissociation curves, gypsum— β -calcium sulphate, and gypsum— γ -calcium sulphate, no longer constitute univariant systems. With the appearance of one additional phase, if this represents an equilibrium condition, the system would become invariant, and would then be a transition point—at which the three solid phases and the vapor would coexist. A change in temperature would then necessitate the disappearance of one solid which becomes unstable in the direction of the change. For gypsum to “dissociate” to either β - or γ - CaSO_4 would require the disappearance of the intermediate compounds, and since this takes place after gypsum itself has disappeared, there is therefore no possibility for gypsum to form a dissociation pressure with either β - or γ - CaSO_4 . The only dissociation pressure that can exist in this case is one for gypsum—hemihydrate.

The idea that a hydrate need not always dissociate in such a way that the next lower hydrate is formed, but may dissociate directly to some lower step, apparently gained general acceptance through the misunderstanding of an expression derived by Ostwald¹⁴ which shows the relationship of such dissociation pressures. Ostwald's assumption of a direct dissociation to that lower step, and the possibility of calculating the value of its dissociation pressure by means of his expression, seems to have been taken generally for proof of its actual existence. Such a dissociation has never been experimentally realized, however, and all reliable experimental evidence uniformly shows that, for a series of hydrates, the dissociation always results in the formation of the compound that is next in its composition. Furthermore, it can be shown¹⁵ from consideration of phase relations that the two substances which give the dissociation pressure that Ostwald had assumed, would both be unstable under these conditions, and that it would be necessary then to assume the velocity of the unstable dissociation reaction to be practically infinitely greater than the reac-

¹⁴ Ostwald, W.: *Lehrbuch d. allgemeinen Chemie*, II, 2, p. 538. W. Engelmann, Leipzig, 1912.

¹⁵ For a more detailed discussion the reader is referred to an article to be published elsewhere.

tion leading to the formation of the stable intermediate compound. For if this were not the case, and a detectable amount of the stable phase were present, the system would no longer be univariant and no dissociation pressure could exist. It may therefore be concluded that the fact that it is possible to calculate values for some assumed dissociation, from the data of related known dissociations, in no way proves this dissociation to be realizable under these conditions, or that it even need exist.

It is possible that van't Hoff mistook Ostwald's statement for proof that a substance may actually dissociate in different ways, and he doubtless assumed also, as is apparently generally assumed, that in all cases involving hydrates there must exist a dissociation pressure curve which terminates at the respective transition point. With these ideas firmly accepted, it is probably not surprising that the experiments with commercial plaster mentioned above, which showed that in the presence of salt solutions, anhydrite and supposedly also "soluble anhydrite" were formed well below the transition of gypsum to hemihydrate, led van't Hoff and his associates to believe that they had proof that gypsum was dissociating directly to either anhydrite or "soluble anhydrite" without going through the formation of the intermediary compounds. The theoretical difficulties which arise with the assumption that gypsum can dissociate in several ways apparently have not been sufficiently considered. At each transition point the dissociation pressure must then be equal to the vapor pressure of the saturated solution. But if the dissociation pressure of gypsum were equal to the vapor pressure of the solution at its transition to anhydrite, it must beyond this point become greater than the vapor pressure of the solution, as otherwise no transition could take place. At the transition point to hemihydrate, at the higher temperature, gypsum, however, must again have a dissociation pressure that is equal to the vapor pressure of its solution. It is not only theoretically necessary, but also a well-established fact, that the vapor pressure of such solutions increases with temperature, irrespective of whether the solubility of the solid phase (binary compound) increases or decreases with the temperature, as that can affect only the slope of the vapor pressure curve.¹⁶ How, then, can the same gypsum have a dissociation pressure equal to the vapor pressure of its saturated solution at the upper

¹⁶ The only exception to this takes place when the solubility curve passes through the congruent melting point of the solid, after which the vapor pressure decreases, but such a case does not enter the present discussion.

transition, when even at the much lower temperature, after passing its transition to anhydrite, it had to develop a dissociation pressure that surpasses the vapor pressure of its solution? The ability to realize the higher transition would require that the dissociation rate for the lower one be infinitely small. It would further require one to assume that, though dissociation usually increases very rapidly with temperature and had to have a higher absolute value, in this case, it still must remain undetectable at the upper transition point, for otherwise the latter could no longer be an invariant point. It seems necessary to conclude either that the lower transition point would never be attainable, or that the upper transition could never be realized, and that actual realization of both transitions based on the dissociation of gypsum is impossible.

The proof that gypsum dissociated directly to anhydrite was thought by van't Hoff and his associates to be furnished by experiments in which gypsum made from commercial plaster of Paris in the presence of salt solutions was converted to anhydrite at temperatures below the transition point of gypsum—hemihydrate. But these experiments prove directly only that the transition gypsum—anhydrite takes place at a lower temperature than the transition gypsum—hemihydrate, and that, therefore, anhydrite above its transition point with gypsum is the stable phase in the system, $\text{CaSO}_4\text{—H}_2\text{O}$, and hemihydrate and “soluble anhydrite” are unstable phases. The solubility of a stable phase is lower than that of an unstable phase, and therefore if both are brought together in contact with solution, the stable will grow at the expense of the unstable. This process generally consists in that the unstable goes into solution, and from the supersaturated solution the stable phase crystallizes out. Gypsum shows a perfectly normal behavior, that is, its solubility is considerably greater than that of anhydrite above their transition point, and therefore crystallization of the stable phase would take place through the medium of solution.

It should be recalled that van't Hoff and associates said that ordinary gypsum, after standing for weeks in contact with salt solutions, never changed to anhydrite, but only to hemihydrate, and that it was essential for the supposed dissociation to anhydrite to use a commercial product. The reason why ordinary gypsum in salt solutions is readily dehydrated to hemihydrate is that its dissociation pressure is lower than the vapor pressure of the salt solutions. On the other hand, in the case

of anhydrite when the commercial product was used, no dissociation need have taken place but a recrystallization through the medium of solution, owing to the presence in this material of nuclei of the stable anhydrite phase, for otherwise, suitable preparations of gypsum, of unquestionable purity and homogeneity, would easily have been found to show similar behavior, and that was clearly not the case. Experiments made by the writer in this connection showed that gypsum had not changed in contact with its solution at 75° after two years, but in a parallel experiment where a small amount of anhydrite had been added, the solid, as would be expected, was found to consist only of anhydrite. Further, X-ray examinations of two commercial plasters of Paris showed in both cases easily detectable amounts of anhydrite, and it seems more than probable that all commercial products would contain at least some nuclei of anhydrite. Obviously, then, the experiments of van't Hoff et al. present no direct proof for the ability of gypsum to dissociate to anhydrite directly, but are based purely on the assumption that such a dissociation pressure should exist, and their experimental work is based entirely on this assumption. As would be expected, it is exceptionally well reasoned, and appears therefore very convincing, but a closer study indicates ample opportunities for delusion. Their data were obtained from measuring very small dilatometric changes which, over long periods of time, were only indicating the trend of the supposed dissociation reaction. Van't Hoff and his coworkers apparently did not consider that besides the formation of anhydrite in their dilatometer, hemihydrate would no doubt also be formed by dissociation of gypsum in the salt solutions; and it is probable that it was the reversibility of this reaction that was indicated by the observed trends of the dilatometer readings, which they took as proof of having approached equilibrium from both directions in the supposed dissociation of gypsum to anhydrite. Their determination of this transition point is clearly not well founded, and the dissociation pressure curve when gypsum goes over into "soluble anhydrite" (γ -CaSO₄) is obviously erroneous. We have mentioned already the ease with which γ -CaSO₄ takes up water from the atmosphere, and changes to hemihydrate. It may now be added that γ -CaSO₄ has recently been found to be a more efficient drying agent than concentrated sulphuric acid,¹⁷ and

¹⁷ Hammond, W. A., and Withrow, J. R.: *Ind. Eng. Chem.*, 25, 653, 1933; Bowers, J. H.; *Bur. Standards J. Research*, 12, 241, 1934.

it remains effective even at 100° . Obviously, then, it is impossible that the transition point, gypsum— $\gamma\text{-CaSO}_4$, could lie at 93° and a vapor pressure of 588 mm., as was found by van't Hoff and his coworkers. Like some other investigators, they had probably mistaken the formation of hemihydrate in their salt solutions for $\gamma\text{-CaSO}_4$.

As unfounded as the assumption of the possibility to realize for a substance different dissociation reactions under the same thermodynamic conditions is the notion that a dissociation pressure curve must terminate at every transition point involving a hydrate. According to the phase rule, the transition point in a two-component system is a quadruple point—a point at which two solid phases coexist with their saturated solution and the vapor phase. Thus every intersection of two solubility curves forms a transition point. Only when between the two solids and the vapor there exists a reversible reaction resulting in the formation of a univariant system, is the transition point the locus of an actual dissociation pressure curve. When this is the case, the transition point is an incongruent melting point, as the dissociation pressure at this point becomes equal to the vapor pressure of the solution saturated in respect to both solids, and therefore formation of the liquid phase at the expense of the higher hydrate must take place. But not every transition point involving a hydrate need necessarily be an incongruent melting point, as seems to be generally assumed. When, as in the present case, the two solids cannot form with vapor a univariant system, because of formation of one or more intermediate reaction products, no dissociation pressure curve can terminate at their transition point. For this reason no incongruent melting takes place, and the change from one to the other solid goes through the medium of solution. This type of transition will always be met when, besides a hydration series in which the individual members originate directly from one another by loss of water, there exists in the same system also a compound (or another series) which is probably in its structure essentially different, and is linked with the first by some form of polymorphism.

SOLUBILITY OF THE SOLID PHASES IN THE SYSTEM,
 $\text{CaSO}_4\text{—H}_2\text{O}$, AND THEIR RELATIONS.

The above conclusions regarding the existence of two distinct types of transition points, which may be encountered when

dealing with hydrates, show that only in the case of one of them does a dissociation pressure curve terminate at this point, and can be used for its location. In the other type no dissociation reaction exists, and the only way to locate the transition point of the two solids is by the generally applicable method of determining the intersection of their solubility curves. The transition point, gypsum—anhydrite, is of this second type, and this is the reason why van't Hoff's vapor pressure experiments led to an erroneous result.

The solubility of gypsum has been very carefully determined by Hulett and Allen,¹⁸ who found that the values given by most earlier investigations were too high, owing to supersaturation resulting from small particle size. In an earlier paper, Hulett¹⁹ showed that solubility values for gypsum may be as much as 20 per cent too high when extremely finely divided material is used, and therefore they carried out their solubility determinations on gypsum using plates of selenite which were freed from fine particles by washing, and to avoid abrasion they stirred only the solution above these gypsum plates. Since this procedure could not be followed throughout the present investigation, it was desirable to determine what differences may be found when ordinary powdered material is used, and the saturation of solutions carried out in the usual way by turning the bottles in the thermostat. Preliminary experiments gave high solubility values which, however, were found to be caused by faulty filtration when Gooch asbestos filters were used. It seems possible that some of the high values obtained by earlier investigators were not always caused by supersaturation, but by the taking, in some cases, of samples without filtration of apparently perfectly clear settled solutions, which the present experience shows may hold some of the very fine particles in suspension. When silica filters of fine porosity were used in filtration the difficulty appeared to be removed, and solubility values were obtained which below 50° were identical with those given by Hulett and Allen. It seems, therefore, that while fine particles may no doubt cause considerable supersaturation, abrasion from turning the bottles is not serious, and the rate of recrystallization of gypsum is high enough to permit the establishment of correct solubility values, provided sufficient time is allowed for attaining equilibrium. The solubility values above 50° were found consistently to be

¹⁸ Hulett, G. E., and Allen, L. E.: *J. Am. Chem. Soc.*, 24, 667, 1902.

¹⁹ Hulett, G. E.: *Z. phys. Chem.*, 37, 385, 1901.

about 3 per cent higher than those of Hulett and Allen. Their solubility value for gypsum at 100° is practically identical with that for hemihydrate, which, as we shall see below, is the stable phase at this temperature. It seems certain, therefore, that equilibrium had not been attained, and the solution, at least in this case, had not reached saturation. That gypsum in contact with its solution was converted at 100° to hemihydrate was first stated by Davis,²⁰ and more recently confirmed by Partridge and White.²¹ This directly contradicts the statement made by van't Hoff and his associates that hemihydrate was not formed from gypsum in boiling water, and that their transition point lies at 107° . Although they arrived at this temperature by an indirect method, their experiments seemed very precise and convincing, since they showed that equilibria were approached from both sides. In view of the importance of obtaining certainty regarding this point, and the ease with which it can be checked, the experiment was again repeated. Coarsely powdered selenite was heated with water in a flask, provided with a condenser, on an electrically heated air-bath. Provision was made to prevent superheating, and readings of the temperature of the solution were no higher than 100.5° . Within about two days the gypsum had been completely converted at this temperature into needle-like crystals of hemihydrate that were about 2 mm. in length. Their growth during this time, and the disappearance of gypsum could readily be observed. The crystals were separated by quickly pouring off the solution, followed by washing them off with acetone, and were readily identified as hemihydrate. The repeated confirmation of the formation of hemihydrate from gypsum at boiling temperature shows the statement of van't Hoff and his associates to be untenable. It is necessary to accept the conclusion that, despite the apparently excellent experimental evidence, showing high precision, van't Hoff's indirect determination of the transition of gypsum to hemihydrate resulted in too high a value.

Partridge and White²² determined the solubility curve of hemihydrate from 98 to 200° , and pointed out that the data given by Hall, Robb, and Coleman,²³ as well as earlier investigators whom they cite, though mistakenly ascribed to "soluble

²⁰ Davis, W. A.: *J. Soc. Chem. Ind.*, 26, 727, 1907.

²¹ *Op. cit.*

²² *Op. cit.*

²³ Hall, R. E., Robb, J. A., and Coleman, G. E.: *J. Am. Chem. Soc.*, 48, 927, 1926.

anhydrite," are in excellent agreement with their values. From the intersection of the solubility curve of hemihydrate with that of gypsum, they gave the transition point as 98° , and by using the solubility data for gypsum given in the present paper, the intersection, as shown in Fig. 2, is found only half a degree lower. The temperature of $97^{\circ} \pm 1^{\circ}$ for the transition point, gypsum—hemihydrate, can be considered securely established.

Partridge and White also determined the solubility of β - CaSO_4 (anhydrite) between 100 and 200° , and making use of a determination by G. L. Haddon and M. W. A. Brown at 33° , concluded that the transition point, gypsum— β -calcium sulphate, lies near 40° and not at 63 - 66° as given by van't Hoff. In a very recent paper, Hill²⁴ gives the solubility of β - CaSO_4 for several temperatures below 100° , and finds that a curve put through these points intersects the solubility curve of gypsum at 42° . He calls attention to the fact that even when a long period of time—four months—is allowed for reaching equilibrium, solubility determinations may differ as much as 5 per cent, depending on whether the approach is made from supersaturation or undersaturation, the former giving high and the latter low values. The data of Partridge and White for the solubility of anhydrite between 100 and 150° are consistently lower than those given by Hall, Robb, and Coleman, but at higher temperatures practically identical values were obtained in both investigations. The time allowed for coming to equilibrium was in both relatively short—mostly less than twelve hours. The agreements at higher temperatures suggest that attainment of equilibrium was probably facilitated at these temperatures by the greater rate in recrystallization, and therefore also of solution. At lower temperature more time may be expected to be required for this, and low values may be caused by insufficient time to reach saturation when coarsely crystalline material is used, while high values may possibly result from insufficient time for recrystallization of some very fine particles, which, if fine enough, may pass through the filter when samples are taken. Experience gained in determining solubility of gypsum mentioned above strongly indicated the latter possibility. In the present experiments, differences in solubilities under apparently identical conditions were found for various samples of anhydrite. Coarsely crystallized natural anhydrite gave low values, and the solubility values for artificial anhydrite, made by heating gypsum, were usually

²⁴ Hill, A. E.: J. Am. Chem. Soc., 59, 2242, 1937.

higher, the lower the temperature to which it had been heated. It was thought that anhydrite made at low temperatures, though aggregated, would consist of very fine primary particles, which may readily disperse in solution and then pass through the filter, giving apparent higher solubilities. This, however, was not definitely established, and since the differences were not great enough to cause any uncertainty in locating the solubility curve

TABLE II.
Solubility Determinations.

Expt	Temp. °C.	Time	Grams CaSO_4 per 100 grams H_2O	Starting materials
<i>Solid phase: gypsum</i>				
23	0	10 days	0.175	Gypsum ¹
21	24	7 days	0.207	"
18	24	11 days	0.207	"
36	38	2 days	0.210	"
36a	38	3 days	0.210	"
19	50	8 days	0.208	"
22	50	10 days	0.208	"
44	51	1 year	0.209	"
45	51	1 year	0.206	"
35	60	15 days	0.202	"
38	60	15 days	0.203	"
47	72	2 years	0.198	Selenite ²
48	72	2 years	0.198	"
32	75	22 days	0.192	Hemihydrate ³
41	92	13 days	0.175	Gypsum ¹
41a	92	23 days	0.179	"
<i>Solid phase: hemihydrate</i>				
26	100.5	2-3 days	0.160	Selenite ²
<i>Solid phase: anhydrite</i>				
28	26	11 days	0.253	Anhydrite ⁴
52	30	10 days	0.243	Natural anhydrite ⁵
53	37	6 days	0.219	"
54	37	7 days	0.234	Anhydrite ⁴
39	47.5	17 days	0.199	"
37	60	13 days	0.156	"
50	72	2 years	0.136	"
58	85	1 year	0.105	Anhydrite ⁴ and small amount of selenite ²
56	85	1 year	0.103	Anhydrite ⁴
42	92	29 days	0.091	"

¹ J. T. Baker, calcium sulphate, C.P.

² Clear plates of selenite, Wayne County, Utah.

³ Made from selenite by heating with water at 100.5°.

⁴ Made by heating gypsum a few hours at about 500°.

⁵ Anhydrite from Midland, California.

for the purpose of the present investigation, only attempts to minimize the possible differences were made, by allowing long periods of time for reaching equilibrium, and by using sintered silica filters of fine porosity for taking samples.

As in the determinations of the solubility of gypsum, samples of solutions were always taken at the temperature of the experiment. After allowing a short time for the solid to settle, the

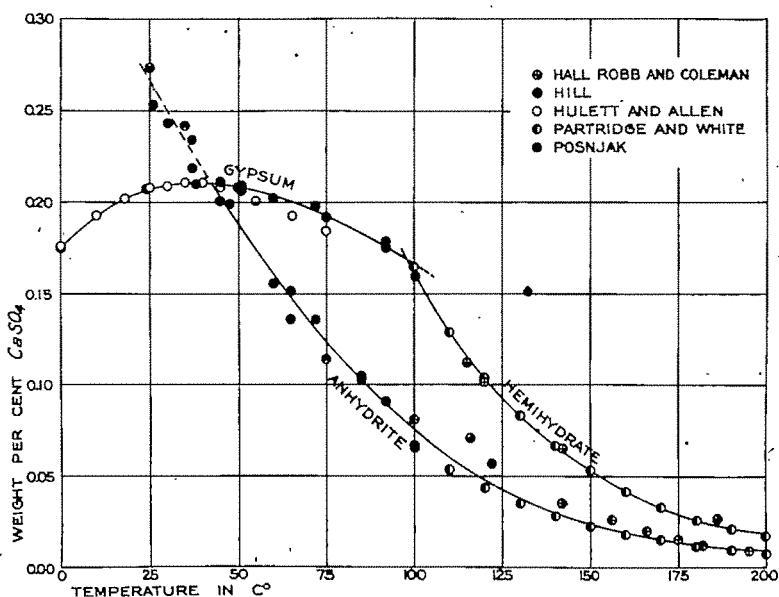


Fig. 3. Solubility of gypsum, hemihydrate, and anhydrite.

stopper of the bottle was replaced quickly by one enclosing the stem of a small immersion filter which was connected to the stopcock of an evacuated bottle. By opening the stopcock the desired amount of solution was slowly sucked into the evacuated bottle. The experimental data are given in Table II. In Fig. 3 the solubility values for anhydrite obtained in all the investigations mentioned above are shown, and, as will be seen, they lie close around a curve that intersects the solubility curve for gypsum at 42° , the temperature given by Hill for the transition point, gypsum—anhydrite, and this temperature is probably correct well within two degrees.

In regard to the transition point, hemihydrate— γ -calcium sulphate, and the solubility of γ - CaSO_4 no definite informa-

tion is available. The ease with which γ -CaSO₄ takes up water vapor to change to hemihydrate shows that the dissociation pressure is very low, and that their transition point lies probably at a fairly high temperature. Attempts made to determine this dissociation pressure curve by direct measurements were unsuccessful, owing to their instability: even below 100°, formation of anhydrite was found to take place slowly, and no reliable values could be obtained, as the requirement for dissociation of a three-phase system was no longer fulfilled.

CONCLUSIONS REGARDING THE DEPOSITION OF ANHYDRITE.

The fact that anhydrite does not form directly from gypsum by dissociation, and that their transition temperature is therefore not affected by the vapor pressure of solutions with which they may be in contact, but is governed by their solubilities, has a geological significance in the interpretation of the conditions of their deposition from sea water. The effect of the presence of salt solution, with which it is of course assumed calcium sulphate does not directly react, on the transition temperature of gypsum to anhydrite will depend on the change in the solubilities of the two solids in such solutions. Three possibilities may be foreseen to result from the presence of salts in the solution. The first is when the solubility of each is either increased or decreased in a relatively equal amount, and their transition temperature will be left unaffected. The second is when the solubility of gypsum is increased relatively more than that of anhydrite, and this will result in lowering the transition temperature. The third possibility, which, however, is probably less likely to take place, appears when the solubility of anhydrite is increased relatively more than that of gypsum, resulting in a raising of the transition temperature. It should be noted that it is the relative change in the solubility of the two solids, and not the absolute amount that is important in affecting the transition temperature. Furthermore, it may be pointed out that in general the angle of the two intersecting curves is of much importance, as it determines how much the transition temperature will be affected by a relative change in the two solubilities. Even a small change in the relative solubilities may therefore produce a surprisingly large effect on a transition temperature.

No data are available for the solubilities of gypsum and anhydrite in sea water at various temperatures. It is known,

however, that the presence of sodium chloride increases the solubility of calcium sulphate very much. On the other hand, sulphates decrease the solubility because of the effect of the common ion. Hill²⁵ determined the solubilities of gypsum and anhydrite in three concentrations of potassium sulphate—from zero to 0.12 per cent—at 35°, and, as the values for each lie on a straight line, he used them to extrapolate the solubilities in pure water. These lines are not parallel, as will be seen from Fig. 4, where Hill's data are plotted, but show that in potassium sulphate solutions the solubility of anhydrite is more

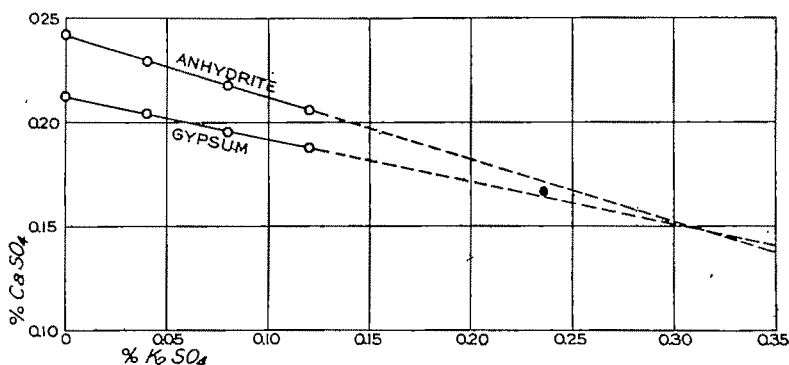


Fig. 4. Solubilities of gypsum and anhydrite in solutions of K_2SO_4 at 35° from data of A. E. Hill.

repressed than that of gypsum. When these lines are extended beyond the experimental data to higher concentrations of potassium sulphate, as shown in Fig. 4, it is found that they will intersect when the solution of K_2SO_4 reaches a concentration of 0.32 per cent. This intersection shows, of course, that in a solution of the above concentration of K_2SO_4 the transition temperature has been lowered about 7° to the temperature of 35°. The vapor pressure of the solution is only insignificantly lowered by the additional amount of dissolved material, and this therefore shows the effectiveness of only a small change in the relative solubilities of gypsum and anhydrite on their transition temperature. It is probably not unreasonable to expect a considerable lowering, which may possibly bring the transition down to ordinary temperature, to take place in sea water.

²⁵ Op. cit.

Solubility experiments in sea water to ascertain definitely the effect on the transition point are now under way.

According to the data collected by the *Challenger* expedition, the salinity of the waters of the open ocean is very uniform. Considerable differences, however, are found in basins such as the Baltic where the large inflow of fresh water lowers the salinity, and on the other hand, the Mediterranean and the Red Sea, which are nearly enclosed, and where a high rate of evaporation combined with the absence of the inflow of fresh water markedly raises the salinity. Ocean water is not saturated in respect to calcium sulphate, and bottom samples collected by the *Challenger* expedition showed that no deposition of calcium sulphate normally takes place. Thick beds of gypsum and anhydrite of marine origin are common, however, and in the Stassfurt salt deposits anhydrite reaches a thickness of almost 100 meters. The amount of calcium sulphate is entirely out of proportion to its presence in sea water, and van't Hoff²⁶ pointed out that the large amount of anhydrite in Stassfurt could not be accounted for by the evaporation of sea water, but that inflow of calcium sulphate-rich water must be assumed. Geologists considered intermittent replenishment of the water in the evaporating basin, and advanced the so-called bar theory. While this might account for the accumulation of thick deposits, it in no way explained the formation of the anhydrite beds, as long as it was assumed that anhydrite could form only from highly concentrated salt solutions. Apparently it is well known that calcium sulphate is precipitated at ordinary temperature long before the solution reaches such high concentration of sodium chloride. If so, the solubility of calcium sulphate, after first increasing with increasing concentration of sodium chloride, reaches a limit, and may be expected to decrease with further concentration. Whether gypsum or anhydrite will be deposited when saturation for calcium sulphate is reached at a given temperature depends on which will then be less soluble. From the foregoing it is probable that high concentration of salts will not be required to bring the deposition of anhydrite down to ordinary temperature. It is expected that solubility determinations in salt solutions will indicate definitely the ranges of temperature and concentration under which either gypsum or anhydrite may have been deposited from sea water.

²⁶ van't Hoff, J. H.: Zur Bildung der ozeanischen Salzallagerungen, II, p. 42 and p. 72, Braunschweig, 1909.

SUMMARY.

It is confirmed that $\gamma\text{-CaSO}_4$ (suggested for the misnomer "soluble anhydrite") is a definite chemical compound which takes up moisture very readily to change to $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (hemihydrate). The only other two solids existing in the system between 0 and 200° are $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) and $\beta\text{-CaSO}_4$ (anhydrite).

The assumption of van't Hoff and associates that gypsum may dissociate in three different ways, forming hemihydrate, anhydrite, or $\gamma\text{-CaSO}_4$, is shown to be erroneous. Gypsum can dissociate only to form hemihydrate, and their transition point, based on new determinations of the solubility of gypsum, lies at $97.5 \pm 1^\circ$, confirming the work of Partridge and White.

No dissociation pressure curve terminates at the quadruple point, gypsum—anhydrite, which results solely from the intersection of their solubility curves. The temperature of this transition point given recently by Hill at 42° has been confirmed by additional solubility determinations.

Owing to the fact that the only dissociation pressure curve that gypsum has does not reach the value of the vapor pressure of its saturated solution until the temperature of $97 \pm 1^\circ$ is attained, gypsum in contact with its solutions between 42 and 97.5° represents a true metastable system, which in the absence of anhydrite nuclei may persist indefinitely.

The effect of salt solutions on the transition temperature of gypsum to anhydrite is discussed. Contrary to former assumptions, it is shown that the presence of even a very small amount of salt in the solution may lower this temperature considerably. The importance of this fact in geological interpretations of formation of anhydrite of marine origin, and the need of quantitative data for its evaluation are pointed out.

DIRECT MEASUREMENT OF SILICATE HEATS OF MELTING.

HOWARD S. ROBERTS.

ABSTRACT.

The reluctance of most silicates to crystallize when once melted makes it difficult to obtain their heats of melting when using calorimeters operated at room temperatures. It is here shown that with a suitable high-temperature calorimeter we may measure the energy actually absorbed by the silicate in the act of melting, as is often done at low temperatures, and so obtain data of usable precision. Determinations are described using pure K_2SO_4 and somewhat impure Na_2SiO_3 , whose melting points are 1069° and 1089° .

The past two or three years have witnessed a rapidly growing interest in thermochemical investigations in many different fields. At the Geophysical Laboratory, extensive phase rule studies of silicate equilibria have been in progress ever since the Laboratory was established; application of these investigations to geologic problems has brought about a more and more urgent demand for thermal data, particularly heats of melting, which has now to be met. Since existing data are scanty, the present need is not so much for a few determinations of high precision as it is for the ability to obtain data of adequate precision in the majority of cases that present themselves. This consideration is an important factor in the choice of method and equipment.

THE PROBLEM IN GENERAL.

If we plot the internal energy of a pure substance as a function of temperature we obtain a curve like ABCD in Fig. 1; the vertical portion BC represents energy absorbed isothermally during the melting process and is the quantity we want to determine.

If the substance contains a small amount of an impurity that forms a eutectic with it, the energy curve resembles AEE'C'D. A vertical portion EE' appears at the eutectic temperature. It represents the energy needed to melt all the impurity and enough of the pure substance to form a saturated solution, together with a generally much smaller heat of dilution. The initial slope of E'C' is greater than that of AB and increases

i.e. a short digression toward A' before crystallization begins; but once started, crystallization proceeds rapidly to completion.

For determinations with these substances the dropping method affords, probably, the most satisfactory and precise means of tracing the energy curve. The cooling takes place in a calorimeter whose temperature rise gives the difference between the energy content of the sample at the initial temperature, before dropping it into the calorimeter, and that at the final temperature of the calorimeter. Since only differences are given, the energy curve thus obtained represents relative and not absolute values.

The silicates, however, are characterized as a class by extreme undercooling. When once melted, most of them fail to crystallize at all unless cooled very slowly, and the heat of melting remains in the sample because from the energy standpoint, as well as the structural, the sample is still a liquid. For them the dropping method gives only the energy curve of the liquid, curve A'D in the figure, located an undetermined distance AA' above AB. This quantity AA' includes the heat of melting. Several investigators have evaluated it by taking the difference between determinations of heat of solution of the glassy and of the crystalline form in some suitable solvent. The determination is complicated and is particularly subject to uncertainties that are difficult to evaluate.

When all these considerations were taken into account it appeared that it would be a great deal simpler and possibly, in the long run, nearly as accurate to determine the energy actually absorbed by the silicate in the act of melting and to subtract from this the energy needed merely to raise its temperature. In the method adopted the greater part of the energy needed is supplied by an electric heater surrounded by the sample being melted. The method is an old one and the desirability of electric heating has been pointed out by many workers, although few have employed it at high temperatures. White¹ investigated it at this Laboratory as a possible method for specific heats but he abandoned it in favor of the dropping method which, for that purpose, is undoubtedly superior. The most recent application of the heater at higher temperatures seems to be that of Moser,² who has used it very successfully for heat capacity measurements up to 700°.

¹ White, W. P.: *J. Phys. Chem.*, 34, 1121-1136, 1930.

² Moser, H.: *Physik. Z.*, 36, 737-753, 1936.

APPARATUS.

Calorimeter and Jacket.

Figure 2 is a drawing of part of the furnace F with the calorimeter in place. The charge is contained in the Pt crucible

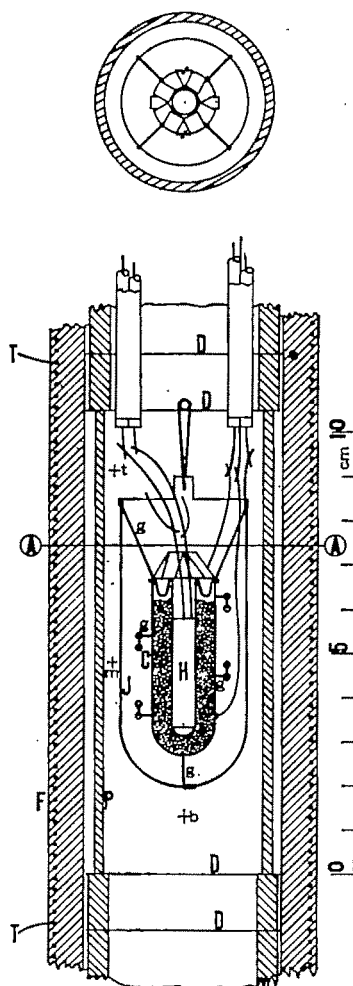


Fig. 2. Calorimeter and part of the furnace. The upper view is a section at the level A-A.

C which is provided with a central well or sheath for the electric heater H. Two lugs at the top of the sheath are bent

outward and welded to corresponding lugs near the top of the crucible. Above this level the crucible is divided into narrow strips by longitudinal saw cuts. After the charge is filled in, these strips are bent inward, leaving a small central opening through which the heater leads pass. The assembly, crucible, sheath, and heater will be referred to as the calorimeter.

The calorimeter is held in position inside the Pt jacket J by 11 guy wires g of 0.2 mm. PtRh. These are spot welded to the outside of the calorimeter and are tied to the jacket by threading through pairs of holes drilled in it. Taken together they form the composite thermocouple which measures temperature difference between calorimeter and jacket and are therefore distributed over the air-gap so as to give an average value of thermal head.

The top of the jacket is cut into strips which, like those at the top of the calorimeter, are bent inward to close the end, leaving 2 small windows for the heater and thermocouple leads.

The jacket hangs in a chamber formed by the porcelain tube P located at the center of the furnace. The ends of the chamber are closed by discs D of thin platinum; and similar platinum discs, alternating with 12 mm. spacers cut from an alundum tube, fill all of the furnace tube above and below the calorimeter chamber.

Furnace and Temperature Regulator.

The furnace core is an alundum tube 394 mm. long, 45 mm. inside, and 57 mm. outside diameter. On this are wound 136 turns of 0.8 mm. Pt wire with a winding pitch of 0.1 inch (2.54 mm.). Electrical leads are brought out from a point on the 43d turn and from a point on the 93d. Thus the winding is divided into a middle section of 50 turns with 2 end sections of 43 turns each. The position of these taps relative to the calorimeter chamber is as indicated at T in Fig. 1. The axial temperature distribution within the calorimeter chamber may be made nearly uniform by adjusting the ratios of the voltages across the 3 sections. The 7 cm. space between the core and the outer case is filled with calcined magnesia for thermal insulation.

The temperature regulator is of the type described elsewhere⁸ but freed of moving contacts by replacing the rectifier, galvanometer, relay, etc. of the 1925 edition with an amplifier and

⁸ Roberts, H. S.: *J Optical Soc. Am.*, 11, 171-186; 1925.

thyatron. A slide wire connected into the regulator, and having its movable contact driven by a synchronous clock motor, provides for heating or cooling at a fairly uniform rate.

Calorimeter Heater.

The heater consists of 35 turns of 0.16 mm. PtRh wire wound on a porcelain tube. The ends of the winding are welded to 0.4 mm. Pt leads, one passing through the center of the tube and the other held by ties of Pt wire in a longitudinal groove in the outside. The heater is insulated from the Pt well by a coating of alundum cement.

It is supplied with low voltage alternating current from a transformer that serves to insulate the heater circuit from the power line. Power is measured by a suspension type dynamometer whose stationary coil carries the whole heater current and whose moving coil is connected through a suitable resistance to potential taps close to the heater.

The heater current produces heat in the leads to the heater as well as in the heater itself. Since the pair of leads runs for 13 mm. through the air-gap, part of the heat produced there is transferred to the calorimeter and the remainder chiefly to the jacket. The calorimeter's share would appear to be somewhat less than half. Accordingly the leads that feed the potential circuit of the wattmeter are welded to the current leads about 5 mm. above the top of the calorimeter. Since the total heat produced in these 26 mm. of current leads is only about 1 per cent of that produced in the heater, the exact location of the potential taps is not very important.

When the heater is first turned on, its resistance increases rapidly and the power would suffer a corresponding decrease if connection were made directly to the transformer. The effect of this increase is minimized by connecting a rheostat in series with the heater and adjusting it, before starting an experiment, to such a value that the heater receives half the voltage of the transformer. When this is done the heater resistance may be changed to 95 per cent or 105 per cent of its original resistance without changing the watts by more than 0.25 per cent.

The energy in joules given to the change by the heater is the integrated product of watts and seconds. Since the voltage of our power supply can be held within 0.1 per cent by a suitable regulator it seemed best in our situation to keep the watts

constant and to record the total time. The laboratory was already provided with a clock that sends out a short electrical impulse each second, and these impulses are used to turn the heater on or off. This requires two quick-acting telephone relays and a switch. When the switch is turned to the "high" position nothing happens until the next impulse from the clock closes the main relay contact, and so connects the heater to the transformer. The relay then remains closed until immediately after the switch is turned back to the "low" position when the contact is opened by the next impulse from the clock. Thus the time of heating is always an integral number of seconds, recorded automatically by an electrical "message counter." The electrical energy that has been supplied to the heater is then equal to the product wattmeter reading \times counter reading.

Since the relay does not open or close instantaneously there is a small error in timing due to the difference between the delay on closing and the delay on opening. Another small error may be caused by electrical transients in the heater circuit at the beginning of each heating period.

For determining the leakage modulus and to reduce the thermal head during determinations of heat of melting, a steady heat is needed of much lower power than that used for melting. This is obtained by having the back contacts of the main relay connect the heater to another transformer of lower voltage. This voltage may be varied by means of an adjustable ratio autotransformer⁴ in the primary circuit. Thus the heater operates at the lower voltage when the main relay is open and at the higher when it is closed.

When both the steady "low" heat and the intermittent "high" heat are used in the same experiment, it is a simplification to treat the high heat increments as superposed on the low. We therefore subtract the low watts from the high and multiply the difference by the counter reading.

Temperature Measurements.

Temperatures are given by the emf's of Pt-PtRh couples measured with a White double potentiometer in conjunction with a sensitive galvanometer. The composite couple for thermal head readings has already been described. The junction giving calorimeter temperature is made by spot welding a

⁴A General Radio Co. Variac.

PtRh wire to the outside of the platinum crucible, the other wire of the couple being a pure platinum wire welded to the top of the crucible. This platinum wire and a similar platinum wire welded to the jacket form the couple for measuring thermal head. Other Pt-PtRh junctions at *b*, *m*, and *t* in the space outside the calorimeter provide for measuring temperature distribution over the length of the calorimeter chamber.

Between the calorimeter chamber and the top of the furnace the thermocouple leads are insulated with porcelain capillaries tied into a bundle and covered with a shield of Pt foil. The shield is connected by a short wire to the top of the jacket and to a similar shield surrounding the four heater leads.

Outside the furnace the single PtRh lead is extended to a glass-enclosed junction with Pt which is immersed in a vacuum bottle filled with ice. This Pt wire and the four coming direct from the calorimeter chamber are joined, inside an isothermal junction box, to the Cu wires leading to the potentiometer.

The whole measuring system is rather^a carefully insulated and shielded^b to minimize effects of electrical leakage. The maximum irregularity in temperature indications, which may originate in the furnace temperature regulator, potentiometer—in fact nearly anywhere in the system—seems to be about $\pm 0.2 \mu\text{v}$ for periods of half an hour or so. For longer periods there are sometimes changes as great as 1 or 2 μv apparently connected with the temperature of the laboratory, as well as a slow downward drift of about 1 μv per day when the furnace stays for long periods in the neighborhood of 1100°.

Thermal head readings made with the furnace temperature stationary about 1100° seem to be free from temporary irregularities greater than 0.1 μv , while the change from day to day appears to be very much less than that of the temperature readings.

DETERMINATIONS WITH SHARPLY MELTING K_2SO_4 .

The first determinations were made with a charge of 7.10 grams of K_2SO_4 . In another investigation^b this material had been found to melt very sharply at 1069°. The energy curve must therefore have nearly the same form as ABCD in Fig. 1. Since K_2SO_4 crystallizes very promptly, determinations could be repeated as needed. The reversible transformation at

^a White, W. P.: J. Am. Chem. Soc., 36, 1856-1885 and 2011-2020, 1914.

^b Roberts, H. S.: Phys. Rev., 23, 386, 1924.

583° was utilized in a study of the calorimeter at this low temperature.

The charge was melted several times under various schedules. Data for two meltings under the schedule finally adopted are plotted in Fig. 3. In these determinations continuous heating by the calorimeter heater was not employed. The furnace was held about 2° below the melting point until temperatures became stationary and then the regulator setting was changed by an amount that would raise the temperature to about 2° above the melting point. While the temperature was rising the thermal head reading was recorded at 15 second intervals and was kept as small as possible by intermittent operation of the heater. The thermal head readings are plotted at I and II in the figure. The data for Curves III- θ and III- ϕ were obtained at a later date with a charge of molten Na_2SiO_3 , but they give an approximate picture of the temperature rise for I and II and of what the thermal head curve might have been if melting had not taken place and the calorimeter heater therefore had not been turned on.

The straight line connecting initial and final values of ϕ in I and II is here assumed to represent, at any temperature, the correction that must be subtracted from the thermal head reading to give the true thermal head. Multiplying the net area between this line and the jagged curve by the leakage modulus k gives the net leakage of energy from calorimeter to furnace. The area, lying below the straight line, represents energy, b , gained by the calorimeter; the area lying above represents energy, c , lost.

If a is the total energy obtained from the heater, then the quantity, $a + b - c$, is the energy retained by the calorimeter and its contents; a part, d , going to raise the temperature of the whole, and the remainder, e , to melting the charge. The part d was taken as the product of temperature rise in μv by the heat capacity C determined at a lower temperature where the amount of melting would be insignificant. Strictly, this value of C is applicable only below the melting point and a different value, to be determined with the charge molten, should be used above the melting point. Over this short temperature interval, however, the difference is negligible.

Thermal head data for a determination of k and C are given as Curves IV- k and IV- C of Fig. 3. In IV- k an input of 13.9 joules per minute (0.232 watts) from the heater caused an increase of 11.1 μv in the thermal head ϕ , the temperature

being stationary at $10227 \mu\text{v}$. At this temperature k is therefore 1.26 joules-per-minute per μv rise in ϕ .

In IV-C a heating rate of $10.1 \mu\text{v}$ per minute caused ϕ to decrease $9.5 \mu\text{v}$, corresponding to an input of 12.0 joules per

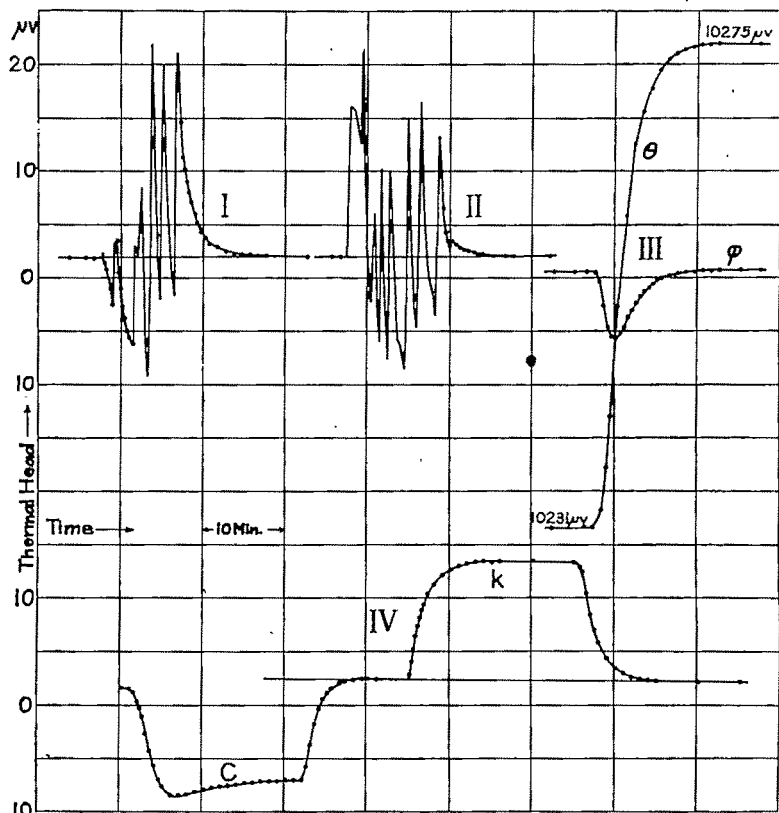


Fig. 3. I, II, IV, thermal head curves for K_2SO_4 . III, thermal head and temperature curves for Na_2SiO_3 .

minute from the furnace, the heater input being zero. In the neighborhood of $10100 \mu\text{v}$, therefore, $C = 1.2$ joules per μv rise in the temperature of the calorimeter. Since the thermal head correction is more uncertain with changing than with stationary temperature, the determined value of C is subject to a greater percentage error than that of k .

Table I is a summary of the quantities measured and calculated in determinations of heat of melting and heat of inversion of the sample of K_2SO_4 .

TABLE I.
 K_2SO_4 Latent Heats.

		Melting		Inversion		
k, joules/min. μv		1.26		0.4		
C, joules/ μv		1.2		0.95		
Final temperature	μv	10411	10411	5101	5108	5104
Initial temperature	μv	10367	10363	5032	5036	5032
Temperature interval	μv	44	48	69	72	72
Watts in heater		5.71	8.76	7.75	9.53	1.18
Seconds heater was on		258	168	43	40	289
a, Input from heater	joules	1473	1471	333	381	323
b, " " furnace	"	27	35	6	0	9
Total input	"	1500	1506	339	381	332
c, Loss to furnace	"	64	72	10	48	3
d, To raise temperature	"	49	53	65	68	68
e, Balance, latent heat for 7.10 g.		1387	1381	264	265	261
Mean ΔH		-195 joules/g.		-37.0 joules/g.		
		-46.5 calories/g.		-8.8 calories/g.		
Estimated uncertainty		2%		7%		

Of the four quantities, *a*, *b*, *c*, and *d*, whose algebraic sum is the heat of melting, *a* has by far the least absolute uncertainty, since it is the product of electrical watts and time. Frequent checking of the wattmeter over a two-month period disclosed an irregular variation less than 0.2 per cent of full scale deflection. The nature of the timing error has already been discussed; it may here be as large as 0.01 second in each of perhaps 20 intervals.

The significant uncertainty of *b* and *c* comes from the choice of thermal head correction used in determining *k*; the uncertainty is probably considerably less than 10 per cent. The thermal head correction is still more uncertain in determinations of *C*, and since the value of *k* is included in *C*, we may expect a possible uncertainty of 20 per cent in the quantity *d*.

In estimating the uncertainty of the final result we must expect that occasionally the contributing errors may all have the same sign. The estimated uncertainty given in Table I is therefore the sum of the individual estimates taken without regard to sign.

The uncertainty introduced by use of the factor *C* might have been avoided if *C* had been determined by following the procedure used for the latent heat determination. At the end of the latter determination the regulator might again have been

set forward so as to cause the temperature to rise through a second interval of the same length as the first. We should then have obtained a thermal head curve similar to III- ϕ in Fig. 3. The thermal head corrections should be very nearly the same for the new as for the original interval. Then, if we imagine this new thermal head superposed on the original curve (Curve I or II in the figure), it can easily be shown that the area between the new curve and the old would have given at once, when multiplied by k , the whole of the correction $b-c-d$ to be added to the electrical input. This method of estimating the correction would have been more satisfactory than the method that was actually employed. It is, in principle, what was employed in the following investigation of impure Na_2SiO_3 .

DETERMINATIONS WITH IMPURE Na_2SiO_3 .

Application of the method to somewhat impure material was studied with a 4.91 gram sample of Na_2SiO_3 that contained a small excess of silica. Since this heat of melting is to be determined in the near future with a much purer sample of Na_2SiO_3 , the present investigation is to be considered as merely a critical study of the method to be used in the actual determination.

The charge was found to crystallize readily when cooled to 950° and it apparently reached an equilibrium between crystals and liquid when held at this temperature over night.

The preliminary study showed that measurements would need to be made over a wide temperature interval and that, for such an interval, we should not be justified in taking the thermal head corrections from a straight line drawn as it was in the K_2SO_4 determination. Since there appears to be no way to determine the magnitude of the correction, except at constant temperature, it was eliminated by running a duplicate experiment with the charge molten and subtracting the thermal head readings so obtained from the corresponding readings obtained with the charge in the act of melting.

The data for Fig. 4 were obtained with the temperature regulator automatically raising the temperature at a rate that varied from $9.7 \mu\text{v}$ per minute at the lowest temperature to 10.6 at the highest. A mistake (now remedied) in the design of the regulator limited the temperature interval that could be covered in a single run to about $600 \mu\text{v}$, so the data had to be obtained in two stages.

The charge was held over night at the initial temperature for the run and at a definite time the next day the regulator was started raising the temperature; about 20 seconds later enough power was turned into the calorimeter heater to bring the thermal head reading to a low value. The "steady heat" was

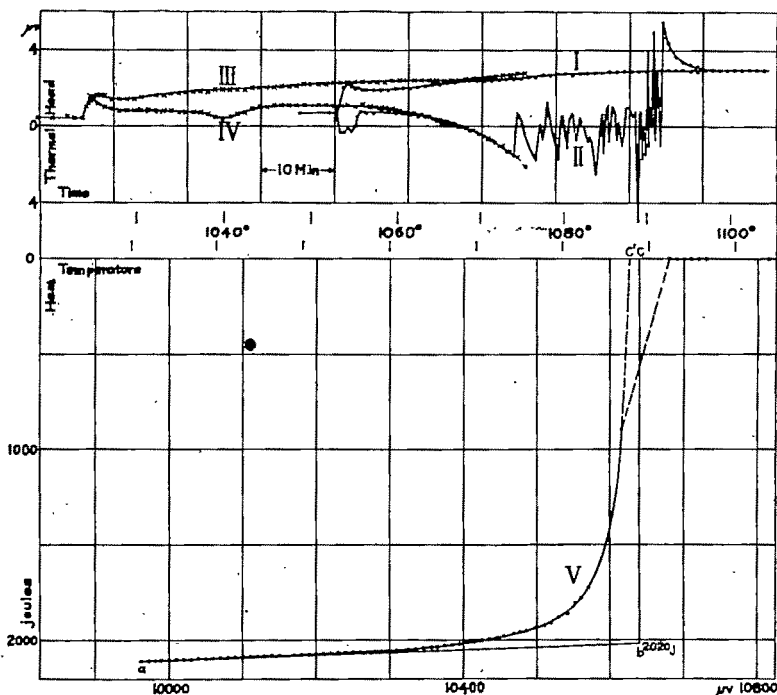


Fig. 4. Thermal head and energy curves for Na_2SiO_3 with small excess SiO_2 . The energy curve differs from the curves of Fig. 1 in that ordinates here represent differences between the total energy of the melting charge and that obtained in a second experiment with the charge still molten. The ordinate Cb, divided by the weight of the charge, is taken as the latent heat of melting. This value, 412 joules per gram, may need considerable revision when the latent heat of the pure compound is determined.

then maintained at its initial value (0.160 watts) throughout all four runs. During the period of rapid melting (Curve I in Fig. 4) additional large increments of energy were put in exactly as was done during the melting of K_2SO_4 . Thermal head data so obtained are plotted in Fig. 4, Curves I and III being for the solid, II and IV for the liquid. The distance from I to II, or III to IV, along any ordinate represents the

difference between the two leakage rates at corresponding times. The area enclosed between these two curves and any two ordinates gives, when multiplied by the leakage modulus, the difference between the total energy received from the furnace by the melting charge and that received by the molten charge, while passing through a particular temperature interval. To this are to be added such increments of energy as may have been received during the same interval from the heater. (The steady heat does not contribute to the difference.) Energy data for Curve V were obtained in this way, omitting the data obtained during the first 10 minutes of each run.

Curve V corresponds to what would be obtained in Fig. 1 by subtracting the ordinates of A'D from those of $aC'D$. The tangent ab at the beginning of the curve corresponds to ab in Fig. 1 and the 1089° ordinate to T_mC . Since we have no data for the pure solid, the curve corresponding to AB of Fig. 1 cannot be included in Fig. 4 and we must take the intercept bC as the heat of melting.

The undetermined quantity corresponding to Bb in Fig. 1 must usually remain undetermined. It is made up of two parts, the heat of melting for the quantity of liquid actually present at a , plus the amount that ab has deviated from AB. Both parts may be diminished by starting at a lower temperature. However, too long an extrapolation of ab may invalidate our tacit assumption of a constant difference between solid and liquid specific heats.

The sources of error in this determination are of the same kind as those already discussed under K_2SO_4 with greater emphasis, however, on those that increase with the temperature interval or with time.

The failure of solid and liquid to attain equilibrium here leads to an uncertainty that may be turned to good account. We have heretofore considered the energy curve as that of the solid and a homogeneous liquid in equilibrium. With rising temperature, however, equilibrium is shifted during the melting process because the newly dissolved solid cannot instantaneously distribute itself through the melt. Thus the quantity of liquid formed is always less than it would be at equilibrium and, during the early part of the experiment, the rate of melting must also be less. Since divergence of ab from AB is proportional to the initial rate of melting, the lower rate leads to a smaller value of the undetermined quantity Bb .

CONCLUSIONS.

Experience gained with these two samples indicates that the apparatus is entirely adequate to supply usable latent heat data for at least a considerable number of the silicates. The difficulty and uncertainty of the determination will undoubtedly increase at the higher temperatures and reach a point where the determination ceases to have any value. There is nothing at present to indicate how far above 1100° this limiting temperature lies; its location will depend to some extent on the nature and purity of the sample to be employed.

It has already been shown that the energy curve in Fig. 4 lies below the curve that would give energy vs. temperature with solid and liquid in equilibrium. However, it was found to be practicable to cover at least part of the melting interval in small steps, measuring energy input and allowing the charge to come to equilibrium between steps. This procedure gives the quantity dQ/dT as a function of temperature and may be useful in investigating processes of solution or dilution.

It may not always be possible to eliminate the thermal head correction by means of a second heating curve with the charge liquid. It appears, however, that the *change* in the correction during the significant part of the experiment may be calculated from measurements of temperature distribution within the calorimeter chamber. In the case of Curves I and III, Fig. 4, this change seems to be about 1/5 of the temperature difference between points t and m in Fig. 2. Additional work is needed to determine the effect of heating rate, especially if the latter is not uniform.

THE SYSTEM, LEUCITE—DIOPSIDE—SILICA.

J. F. SCHAIRER AND N. L. BOWEN.

ABSTRACT.

Several silicate systems have been investigated or are now being studied to ascertain what compositions residual liquids from fractional crystallization approach. The system now presented combines the simple pyroxene, diopside, with potash-alumina silicates. Phase equilibrium data show that diopside is almost quantitatively removed, leaving liquids that approach in composition a mixture of potash feldspar and silica.

INTRODUCTION.

For many years we have been investigating in the laboratory the mutual melting relations of the mineral molecules which constitute the igneous rock magmas. We have been particularly interested in the melting phenomena of the olivines and pyroxenes, which are among the early minerals to crystallize from a cooling magma, and in the alkali-alumina silicates which are among the late minerals.

Recently we have been studying the melting behavior of systems which combine one of the early-formed minerals with late-forming minerals to ascertain the nature of the residual liquids from fractional crystallization of such systems. The system, $\text{NaAlSi}_3\text{O}_8$ — FeO — SiO_2 , with fayalite as the early-forming mineral, and albite and silica or albite and nepheline as the minerals rich in the residual liquids, has already been published¹. Liquidus data for the system, leucite—nepheline—silica, are nearly complete and will be published soon. We now present the equilibrium data for the system, leucite—diopside—silica, which combines one of the simplest pyroxenes, diopside ($\text{CaMgSi}_2\text{O}_6$), with the potash-bearing alkali-alumina silicates, leucite (KAlSi_3O_8), and potash feldspar (KAlSi_3O_8), and with the several forms of SiO_2 .

PREPARATION OF THE TERNARY MIXTURES.

In the preparation of silicate mixtures containing K_2O , special care must be used to avoid loss of K_2O and consequent departure from composition. Several K_2O — SiO_2 glasses with

¹ Bowen, N. L., and Schairer, J. F.: J. Geol., 46, 397-411, 1938.

different K_2O contents were made from $KHCO_3$ and purified quartz. The loss of K_2O is minimized by first sintering at low temperatures and then gradually raising the temperature to about $1400^\circ C$. The small loss was determined by weighings and corrected by adding the appropriate amount of $KHCO_3$.

Diopside was prepared by melting together specially purified $CaCO_3$, MgO , and quartz, and presents no difficulties.

The ternary mixtures were prepared by fusing together in platinum crucibles one of the several K_2O-SiO_2 glasses, specially purified Al_2O_3 , diopside, and quartz. It is necessary to fuse a mixture several (usually five to eight) times, with intermediate grinding, to secure a homogeneous glass. The homogeneity of the glass is checked under the microscope by an absolutely uniform index of refraction of the glass grains.

EQUILIBRIUM STUDIES.

Investigation of the melting relations of the ternary mixtures was carried out entirely by the method of quenching,² which consists in holding a small charge of known composition at a measured temperature for a period of time adequate for attainment of equilibrium between the several phases, and then chilling instantly to room temperature to "freeze" the equilibrium. Quenched charges are examined with a petrographic microscope to determine the nature and number of crystalline and liquid phases. Crystals are identified by their optical properties. On quenching, these liquids "freeze" to a glass.

Special precautions were taken to have only small crystals present in the various mixtures before making the quenching experiments, in order to hasten attainment of equilibrium between crystals and liquid. For those compositions near a boundary curve, care was taken to have both kinds of crystals present in the initial charge.

Equilibrium is reached rather promptly in the ternary system except below 1350° in the leucite field, below 1300° in the tridymite field, and below 1200° in the diopside field. With the exceptions noted, equilibrium is reached in a few hours, although longer times were usually given to be on the safe side.

Quenching experiments were conducted in platinum-wound electric furnaces whose temperature was controlled ($\pm 2^\circ$) with the Geophysical Laboratory furnace thermostat,³ some-

² Shepherd, E. S., Rankin, G. A., and Wright, F. E.: *This Journal*, 28, 308, 1909.

³ Roberts, H. S.: *J. Optical Soc. Am.*, 11, 171-186, 1925.

what modified from the original design but identical in principle.

The temperature was measured with a thermocouple placed nearly in contact with (about 1 mm. distant from) the small charge wrapped in a tiny platinum envelope, which is suspended in that part of the furnace determined as the "hot point." In a well insulated furnace there is a range of about 5 mm. on either side of the "hot point" where the temperature falls off only about one-half degree. The small platinum envelope containing the charge hangs entirely within this zone.

The Pt—Pt 90 Rh 10 thermoelement was calibrated frequently at several fixed points defined in degrees Centigrade as follows:

Anorthite melting point	1550°
Diopside melting point	1391.5°
Li_2SiO_3 melting point	1201°
Gold melting point	1062.6°

THE BINARY SYSTEMS.

The ternary system, leucite—diopside—silica, is bounded by the limiting binary systems, leucite—diopside, diopside—silica, and leucite—silica. There are no binary systems within the ternary system.

The System, Leucite—Diopside.

This system has been described in a previous paper.⁴ Leucite (KAlSi_2O_6) melts congruently at $1686 \pm 5^\circ$ and diopside ($\text{CaMgSi}_2\text{O}_6$) congruently at 1391.5° , and they form a eutectic at 61.5 weight per cent diopside and at the temperature $1300 \pm 2^\circ$. The equilibrium diagram is reproduced in Fig. 1.

The System, Diopside—Silica.

Data for this system are given in two previous papers. Bowen⁵ shows the eutectic relation between diopside and tridymite at 84 weight per cent diopside and at the temperature 1362° . Greig⁶ gives data for the region of two immiscible liquids in the ternary system, CaO—MgO—SiO_2 , from which the binary relations for diopside— SiO_2 may be interpolated. Greig⁷ places the melting point of cristobalite at $1713 \pm 5^\circ$.

⁴ Bowen, N. L., and Schairer, J. F.: This Journal, 18, 301-312, 1929.

⁵ Bowen, N. L.: This Journal, 38, 209-210, 1914.

⁶ Greig, J. W.: This Journal, 13, 28-33 and 36, 1927.

⁷ Greig, J. W.: Op. cit., p. 12.

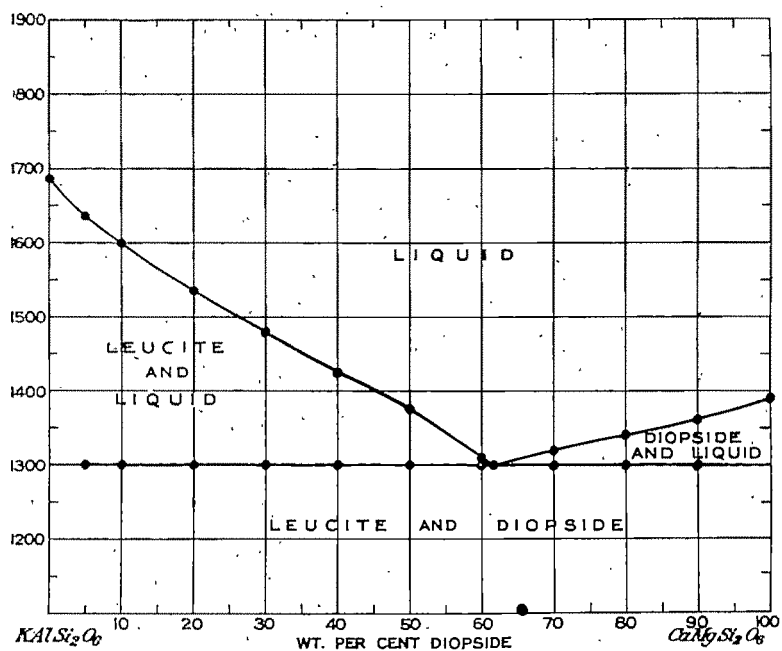


Fig. 1. Equilibrium diagram of the binary system, leucite—diopside (after Bowen and Schairer).

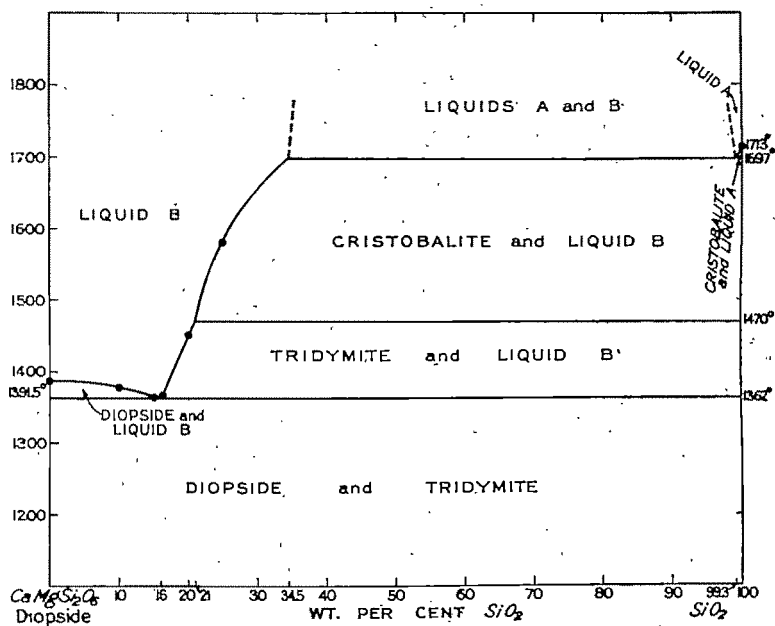


Fig. 2. Equilibrium diagram of the binary system, diopside—silica (after data of Bowen and of Greig).

A diagram for the binary system using the data of Bowen and of Greig is given in Fig. 2.

The System, Leucite—Silica.

Morey and Bowen⁸ give data showing the incongruent nature of the melting of potash feldspar (KAlSi_3O_8) to leucite and liquid, presenting a hypothetical diagram for the system, leucite—silica. As a result of the great viscosity of the mixtures

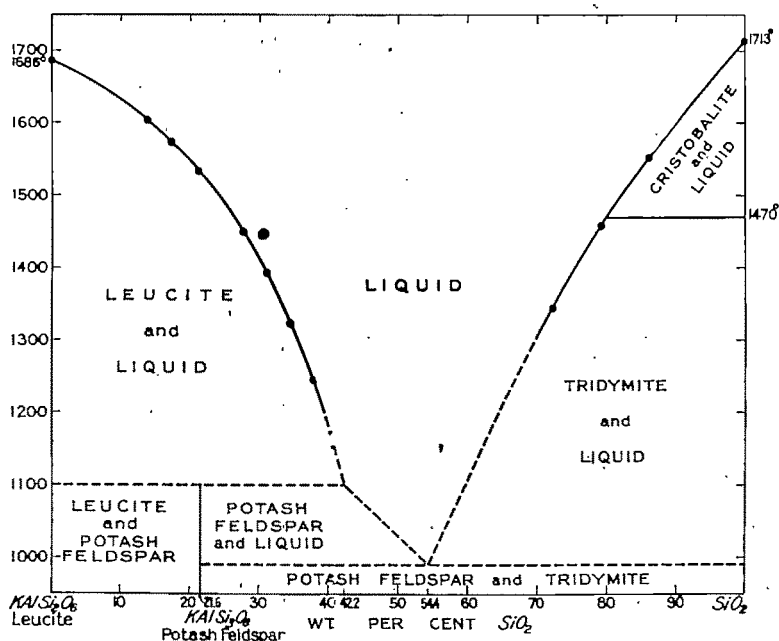


Fig. 3. Preliminary diagram of the binary system, leucite—silica.

and the difficulties in crystallizing them, the best data for this system may be obtained from direct quenching experiments on those compositions rich in leucite and those rich in silica; and from intermediate compositions the best data may be obtained by interpolation from the ternary data in the system, $\text{K}_2\text{O—Al}_2\text{O}_3\text{—SiO}_2$, to be published later.⁹ A preliminary diagram is given here in Fig. 3. The data on which it is based will be

⁸ Morey, G. W., and Bowen, N. L.: This Journal, 4, 1-21, 1922.

⁹ The system, $\text{K}_2\text{O—Al}_2\text{O}_3\text{—SiO}_2$: unpublished work of J. F. Schairer and N. L. Bowen.

given later with those of the system, $K_2O-Al_2O_3-SiO_2$. Broken lines indicate the portions of the diagram based on data from this ternary system.

THE TERNARY SYSTEM.

To determine the liquidus temperatures, the slopes of the liquidus surface and the fields of stability of the primary crystal-

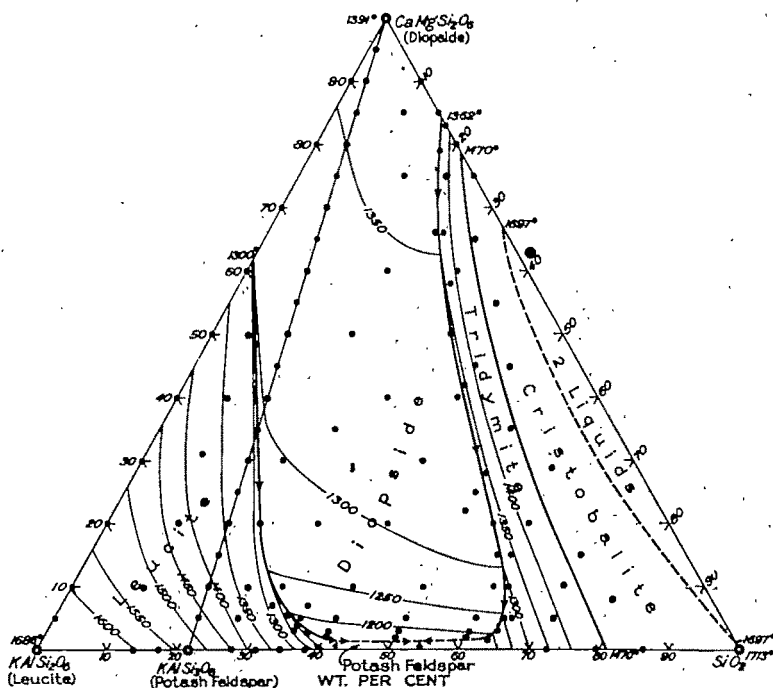


Fig. 4. Equilibrium diagram of the ternary system, leucite—diopside—silica.

line phases with their boundary curves, quenching experiments were made on eighty-nine different ternary compositions. These data are assembled in Table I and presented graphically in Fig. 4. All compositions are expressed in weight per cent. Boundary curves are indicated by heavy lines. Broken lines indicate some uncertainty as to their precise location. Isotherms are given as lighter lines with the temperature indicated on each. The triangle representing the whole system is divided

into two smaller triangles by the line joining potash feldspar and diopside. Black dots represent the eighty-nine compositions actually studied, and double open circles the compositions of compounds. Arrows on the boundary curves indicate the direction of falling temperature.

A noteworthy feature of the ternary system is the extension of the field of diopside from pure diopside itself nearly down to the binary bounding system, leucite—silica. Even with less than two per cent diopside in the total composition of a mixture, diopside may be the first crystalline phase to appear on cooling. For mixtures in this system, diopside is removed, on cooling, almost quantitatively (with some leucite or some silica also for appropriate compositions), leaving a residual liquid which is almost pure potash-alumina silicate in composition.

In many silicate systems, cristobalite often crystallizes and persists metastably for long periods of time at temperatures within the stability range of tridymite. In this ternary system, tridymite always appears in its temperature range of stability and grows beautiful thin hexagonal plates, flattened parallel to the base (0001). If the temperature is raised above $1470^{\circ}\pm$, these readily invert to cristobalite and re-form on holding the temperature for several hours below $1470^{\circ}\pm$.

It will be noted that the field of diopside crowds down so close (to less than two per cent diopside) to the leucite-silica side line that the field of potash feldspar in the ternary system is very small. As has been previously noted, compositions in this region of low temperatures are exceedingly viscous,¹⁰ impossible or almost impossible to crystallize in dry melts and so slow in reaching equilibrium as to be impractical experimentally. The temperatures and compositions of the ternary reaction point and ternary eutectic in the system, leucite—diopside—silica, cannot be much different in temperature or composition from those of the binary reaction point and binary eutectic, respectively, in the binary system, leucite—silica. The best values for these binary points and their compositions will be given with the data on which they are based, when the data for the ternary system, $K_2O-Al_2O_3-SiO_2$ are published.

There are no solid solutions in the system. The optical properties of the crystalline phases agree with those reported in pre-

¹⁰ For data on viscosities of silicate glasses, see N. L. Bowen: *Trans. Am. Geophys. Union*, 15, 249-255, 1934.

TABLE I.
Results of Quenching Experiments.

Refractive index of glass ± .003	Composition in wt. per cent			Temp. ° C.	Time	Phases
	Leucite	Diopside	Silica			
Points on Cristobalite Surface						
1.553	5	65	30	1505	5 hrs.	Small amount cristobalite in glass
				1515	5 hrs.	Very rare cristobalite in glass
1.539	7	55	38	1550	8 hrs.	Rare cristobalite in glass
				1555	8 hrs.	All glass
1.525	10	45	45	1530	4 hrs.	Rare cristobalite in glass
				1535	4 hrs.	All glass
1.503	12	29	59	1540	8 hrs.	Rare cristobalite in glass
				1545	6 hrs.	All glass
1.484	15	15	70	1505	5 hrs.	Small amount cristobalite in glass
				1510	8 hrs.	Very rare cristobalite in glass
				1515	5 hrs.	All glass
1.475	14	8	78	1530	4 hrs.	Rare cristobalite in glass
				1535	4 hrs.	All glass
Points on Tridymite Surface						
1.568	4	75	21	1359	4 hrs.	Very rare diopside and much tridymite in glass
				1395	18 hrs.	Small amount tridymite in glass
				1405	24 hrs.	Very rare tridymite in glass
				1410	48 hrs.	All glass
1.557	9	66	25	1345	5 hrs.	Small amount diopside and moderate amount tridymite in glass
				1347	3 hrs.	Moderate amount tridymite in glass
				1360	20 hrs.	Rare tridymite in glass
				1365	18 hrs.	All glass
1.547	10	60	30	1405	24 hrs.	Rare tridymite in glass
				1410	72 hrs.	All glass

1.546	12	58	30	1340	3 hrs.	Small amount diopside and much tridymite in glass
				1344	3 hrs.	Much tridymite in glass
				1365	18 hrs.	Rare tridymite in glass
				1370	4 hrs.	All glass
1.527	15	45	40	1405	24 hrs.	Rare tridymite in glass
				1410	72 hrs.	All glass
1.523	18	42	40	1325	3 hrs.	Much diopside and tridymite in glass
				1328	4 hrs.	Much tridymite in glass
				1340	17 hrs.	Rare tridymite in glass
				1345	20 hrs.	All glass
1.515	15	35	50	1465	24 hrs.	Rare tridymite in glass
				1470	24 hrs.	All glass
1.505	22	28	50	1335	15 hrs.	Rare tridymite in glass
				1340	17 hrs.	Very rare tridymite in glass
				1345	20 hrs.	All glass
1.493	20	20	60	1410	72 hrs.	Much tridymite in glass
				1416	24 hrs.	Very rare tridymite in glass
				1420	24 hrs.	All glass
1.487	25	15	60	1340	24 hrs.	Rare tridymite in glass
				1345	24 hrs.	All glass
1.480	28	10	62	1290	72 hrs.	Moderate amounts both diopside and tridymite in glass
				1295	24 hrs.	Rare tridymite in glass
				1300	24 hrs.	All glass
1.478	20	10	70	1440	24 hrs.	Small amount tridymite in glass
				1445	24 hrs.	All glass
1.476	31	5	64	1250	24 hrs.	Very rare diopside and moderate amount tridymite in glass
				1260	48 hrs.	Rare tridymite in glass
				1265	72 hrs.	All glass
1.476	30	5	65	1250	72 hrs.	Rare diopside and much tridymite in glass
				1260	72 hrs.	Much tridymite in glass
				1290	19 hrs.	Very rare tridymite in glass
				1295	18 hrs.	All glass
1.475	24	5	71	1395	48 hrs.	Rare tridymite in glass
				1400	48 hrs.	All glass

TABLE I—Continued.

Refractive index of glass $\pm .003$	Composition in wt. per cent			Temp. ° C.	Time	Phases
	Leucite	Diopside	Silica			
1.475	33	3	64	1210	72 hrs.	Very rare diopside and much tridymite in glass
				1225	7 days	Small amount tridymite in glass
1.474	35	2	63	1230	6 days	All glass
				1160	7 days	Rare diopside and much tridymite in glass
				1185	10 days	Rare tridymite in glass
				1190	10 days	All glass
Points on Diopside Surface						
1.603	3.92	*95.00	1.08	1378	4 hrs.	Very rare diopside in glass
1.594	7.83	*90.00	2.17	1382	2 hrs.	All glass
1.588	11.75	*85.00	3.25	1370	4 hrs.	Very rare diopside in glass
1.586	5	85	10	1372	3 hrs.	All glass
1.580	15.67	*80.00	4.33	1359	4 hrs.	Rare diopside in glass
1.573	19.58	*75.00	5.42	1361	3 hrs.	All glass
1.571	10	75	15	1364	4 hrs.	Much diopside in glass
1.567	23.50	*70.00	6.50	1370	4 hrs.	All glass
1.559	10	66	24	1350	3 hrs.	Very rare diopside in glass
				1352	4 hrs.	All glass
				1344	3 hrs.	Rare diopside in glass
				1347	3 hrs.	All glass
				1356	3 hrs.	Moderate amount diopside in glass
				1359	4 hrs.	All glass
				1335	3 hrs.	Rare diopside in glass
				1338	3 hrs.	All glass
				1340	5 hrs.	Moderate amount diopside and rare tridymite in glass
1.562	27.42	*65.00	7.58	1345	5 hrs.	Rare diopside in glass
				1325	3 hrs.	Moderate amount diopside in glass
				1329	3 hrs.	All glass

1.555	31.33	*60.00	8.67	1322	5 hrs.	Rare diopside in glass
1.552	20	60	20	1324	6 hrs.	All glass
1.552	35.25	*55.00	9.75	1344	3 hrs.	Very rare diopside in glass
1.546	39.16	*50.00	10.84	1317	3 hrs.	All glass
1.543	30	50	20	1321	4 hrs.	Moderate amount diopside in glass
1.542	43.08	*45.00	11.92	1309	5 hrs.	All glass
1.533	47	*40	13	1312	5 hrs.	Small amount diopside in glass
1.527	30	40	30	1324	5 hrs.	All glass
1.522	20	40	40	1303	6 hrs.	Small amount diopside in glass
1.522	40	35	25	1307	5 hrs.	Much diopside in glass
1.515	50	30	20	1300	48 hrs.	All glass
1.511	30	30	40	1303	18 hrs.	Small amount diopside in glass
1.500	25	25	50	1320	48 hrs.	Much diopside in glass
1.498	28	22	50	1322	5 hrs.	All glass
1.503	50	20	30	1325	24 hrs.	Very rare diopside in glass
1.500	40	20	40	1330	24 hrs.	All glass
				1310	5 hrs.	Small amount diopside in glass
				1313	5 hrs.	All glass
				1295	18 hrs.	Moderate amount diopside in glass
				1317	18 hrs.	All glass
				1321	4 hrs.	Moderate amount diopside in glass
				1317	5 hrs.	Moderate amount diopside in glass
				1321	5 hrs.	Very rare diopside in glass
				1325	24 hrs.	All glass
				1310	24 hrs.	Moderate amount diopside in glass
				1313	5 hrs.	Rare diopside in glass
				1315	24 hrs.	All glass
				1280	24 hrs.	Much diopside in glass
				1285	24 hrs.	Very rare diopside in glass
				1290	72 hrs.	All glass
				1300	24 hrs.	Rare diopside in glass
				1305	24 hrs.	All glass

TABLE I—Continued.

Refractive index of glass $\pm .003$	Composition in wt. per cent			Temp. ° C.	Time	Phases
	Leucite	Diopside	Silica			
1.488	27	15	58	1305	24 hrs.	Rare diopside in glass
1.495	60	10	30	1310	24 hrs.	All glass
				1230	24 hrs.	Moderate amount diopside in glass
				1235	24 hrs.	Rare diopside in glass
1.493	50	10	40	1240	72 hrs.	All glass
				1250	72 hrs.	Small amount diopside in glass
1.487	40	10	50	1255	24 hrs.	All glass
				1265	24 hrs.	Rare diopside in glass
1.481	30	10	60	1270	24 hrs.	All glass
				1285	72 hrs.	Moderate amount diopside in glass
1.488	58	7	35	1290	24 hrs.	All glass
				1215	48 hrs.	Moderate amount diopside in glass
1.487	60	5	35	1220	72 hrs.	All glass
				1180	7 days	Moderate amount diopside in glass
				1185	10 days	Very rare diopside in glass
				1190	10 days	All glass
1.485	55	5	40	1200	48 hrs.	Small amount diopside in glass
1.483	45	5	50	1205	48 hrs.	All glass
				1215	24 hrs.	Moderate amount diopside in glass
				1220	48 hrs.	Very rare diopside in glass
1.478	35	5	60	1225	24 hrs.	All glass
				1235	24 hrs.	Small amount diopside in glass
				1240	72 hrs.	Very rare diopside in glass
1.484	57	3	40	1245	24 hrs.	All glass
				1150	48 hrs.	Small amount diopside in glass
1.480	47	3	50	1155	6 days	All glass
				1160	4 days	Moderate amount diopside in glass
				1165	5 days	Very rare diopside in glass
				1170	48 hrs.	All glass

1.475	37	3	60	1205	48 hrs.	Rare diopside in glass
				1210	48 hrs.	Very rare diopside in glass
				1215	72 hrs.	All glass
1.483	58	2	40	1080	10 days	Moderate amount diopside in glass
				1090	10 days	Small amount diopside in glass
				1095	10 days	All glass
1.479	53	2	45	1100	7 days	Moderate amount diopside in glass
				1105	7 days	Rare diopside in glass
				1110	7 days	All glass
1.477	48	2	50	1110	7 days	Rare diopside in glass
				1115	7 days	All glass
1.475	38	2	60	1140	7 days	• Moderate amount diopside in glass
				1145	7 days	Rare diopside in glass
				1150	7 days	All glass
Points on Leucite Surface						
1.546	45	50	5	1303	5 hrs.	Rare diopside and much leucite in glass
				1307	5 hrs.	Much leucite in glass
				1315	18 hrs.	Rare leucite in glass
				1320	18 hrs.	All glass
1.535	53	40	7	1345	48 hrs.	Very rare leucite in glass
				1350	24 hrs.	All glass
1.522	61	31	8	1370	48 hrs.	Rare leucite in glass
				1375	48 hrs.	All glass
1.521	54.83	*30.00	15.17	1300	48 hrs.	Rare leucite in glass
				1303	18 hrs.	Very rare leucite in glass
				1305	72 hrs.	All glass
1.513	58.75	*25.00	16.25	1320	4 days	Rare leucite in glass
				1325	7 days	All glass
1.512	70	20	10	1410	48 hrs.	Rare leucite in glass
				1415	48 hrs.	All glass
1.509	62.66	*20.00	17.34	1340	72 hrs.	Rare leucite in glass
				1345	48 hrs.	All glass
1.503	66.58	*15.00	18.42	1365	72 hrs.	Rare leucite in glass
				1370	48 hrs.	All glass

TABLE I—Concluded.

Refractive index of glass ± .003	Composition in wt. per cent			Temp. °C.	Time	Phases
	Leucite	Diopside	Silica			
1.504	80	10	10	1510 1515 1520	5 hrs. 8 hrs. 5 hrs.	Small amount leucite in glass Rare leucite in glass All glass
1.499	70.50	*10.00	19.50	1410 1415	48 hrs. 48 hrs.	Small amount leucite in glass All glass
1.496	65	10	25	1310 1315	4 days 6 days	Small amount leucite in glass All glass
1.490	63	7	30	1280 1285	72 hrs. 24 hrs.	Small amount leucite in glass All glass
1.488	61	6	33	1200 1205 1210	7 days 7 days 7 days	Small amount diopside and much leucite in glass Moderate amount leucite in glass Small amount leucite in glass
1.493	74.41	*5.00	20.59	1215 1465	7 days 24 hrs.	All glass Rare leucite in glass
1.490	69	5	26	1470 1370	24 hrs. 48 hrs.	Very rare leucite in glass Small amount leucite in glass
1.486	61	4	35	1375 1215	48 hrs. 7 days	All glass • Small amount leucite in glass
1.485	62	3	35	1220 1230	7 days 7 days	All glass Small amount leucite in glass
1.484	60	3	37	1235 1160 1165 1170	12 days 8 days 10 days 7 days	All glass Small amount leucite in glass Very rare leucite in glass All glass
1.576	3	79	18	Points on Boundary Curves		
				1361	3 hrs.	Much diopside and much tridymite in glass
				1364	3 hrs.	All glass

1.536	16	50	34	1330	4 hrs.	Much diopside and rare tridymite in glass
1.495	25	20	55	1333	4 hrs.	All glass
				1310	24 hrs.	Moderate amount diopside and small amount tridymite in glass
1.525	50.91	*35.00	14.09	1315	24 hrs.	All glass
1.508	58	20	22	1295	18 hrs.	Rare diopside and very rare leucite in glass
				1300	18 hrs.	All glass
				1265	4 days	Moderate amount diopside and small amount leucite in glass
				1270	4 days	All glass

* Compositions so designated lie on the join, potash feldspar—diopside.

vious papers from this Laboratory.¹¹ At temperatures below about 1200°, diopside tends to form as long needle-like crystals. No further work was done in the region of two immiscible liquids, and for a discussion of liquid immiscibility in the system, CaO—MgO—SiO_2 , the reader is referred to the work of Greig.¹²

THE INVARIANT POINTS.

In the three binary systems bounding the ternary system, there are seven binary invariant points—three of them binary eutectics, one a binary reaction point¹³ (potash feldspar+leucite+liquid), one a binary point of equilibrium between cristobalite, two liquids, and vapor, and two binary transition points of tridymite to cristobalite.

There are two ternary invariant points, one a eutectic between potash feldspar, tridymite, and diopside, the other a ternary reaction point with leucite and potash feldspar as the reaction pair. The phases at the ternary reaction point are leucite, potash feldspar, diopside, liquid, and vapor.

The data for the invariant points are given in Table II.

THE JOIN, POTASH FELDSPAR—DIOPSIDE.

The join, potash feldspar—diopside is a line across the ternary system representing all mixtures of potash feldspar¹⁴ and diopside. It is not binary because of the appearance of leucite crystals whose composition does not lie in this join and the consequent departure of the composition of liquids from this line when the solid phase, leucite, is present. The data (marked with an asterisk in Table I) are plotted in Fig. 5 as a partial representation of the melting behavior of mixtures

¹¹ For diopside, see Ferguson, J. B., and Merwin, H. E.: *This Journal*, 48, 87, 1919.

For leucite, see Bowen, N. L., and Schairer, J. F.: *This Journal*, 18, 308-309, 1929.

For tridymite and cristobalite, see Fenner, C. N.: *This Journal*, 36, 351-356, 1913.

¹² Greig, J. W.: *This Journal*, 13, 28-33, 1927.

¹³ For a discussion of the reaction principle, see Bowen, N. L.: *J. Geol.*, 30, 177-198, 1922.

¹⁴ In this paper, the term potash feldspar is used advisedly for the compound KAlSi_3O_8 ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$). The relations of the two crystalline forms of this compound, orthoclase (monoclinic) and microcline (triclinic), have not been determined. So far, our crystals are too small, or not suitable, to determine which form crystallizes from melts in the ternary system, $\text{K}_2\text{O—Al}_2\text{O}_3\text{—SiO}_2$.

Temp. °C.	Phases
	Unary
1713 ± 5	Cristobalite and liquid SiO ₂ (Greig)
1686 ± 5	Leucite and liquid KAlSi ₃ O ₈ (Bowen and Schairer)
1391.5*	Diopside and liquid CaMgSi ₂ O ₆
	Binary
1300 ± 2	Leucite, diopside, and liquid (61.5% diopside) (Bowen and Schairer)
1362 ± 2	Diopside, tridymite, and liquid (84% diopside) (Bowen)
990 ± 20	Potash feldspar, tridymite, and liquid (unpublished work of Schairer and Bowen)
1100 ± 20	Leucite, potash feldspar, and liquid (unpublished work of Schairer and Bowen)
1698 ± 5	Cristobalite and two liquids (Greig)
1470 ± 10	Tridymite, cristobalite, and liquid $\left\{ \begin{array}{l} 79\% \text{ diopside} \\ 21\% \text{ SiO}_2 \end{array} \right\}$ (Bowen)
1470 ± 10	Tridymite, cristobalite, and liquid $\left\{ \begin{array}{l} 80\% \text{ SiO}_2 \\ 20\% \text{ leucite} \end{array} \right\}$ (unpublished work of Schairer and Bowen)
	Ternary
below 1100°	Leucite, potash feldspar, diopside, and liquid (ternary reaction point)
below 990°	Potash feldspar, diopside, tridymite, and liquid (ternary eutectic)

between diopside and potash feldspar. The diopside liquidus is shown as a heavy line and the liquidus of leucite as a light line. The crystallization of these mixtures is discussed later.

Homogeneous glasses were prepared for the eighty-nine ternary compositions studied, and the index of refraction of each glass was measured at 25° C. with the petrographic microscope by comparison with standardized immersion liquids. The values obtained are given in the first column of Table I. The values are accurate to ± 0.003 . No attempts were made to anneal the glasses or relieve strains. The data are plotted in Fig. 6. The compositions measured are indicated by black dots. Isofracts or curves of equal index of refraction are plotted in the composition triangle.

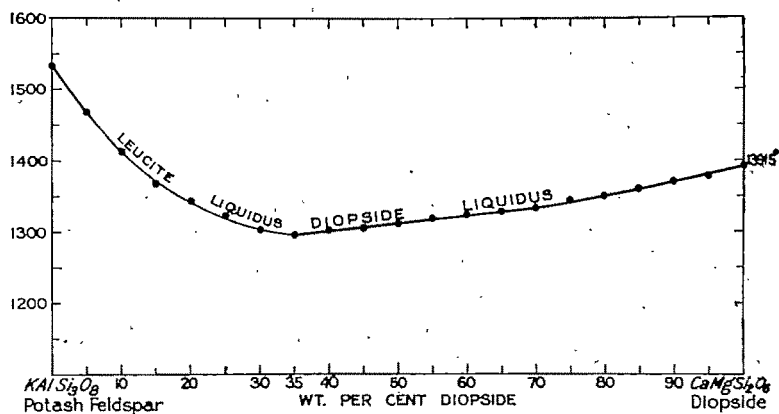


Fig. 5. The join, potash feldspar—diopside (not binary).

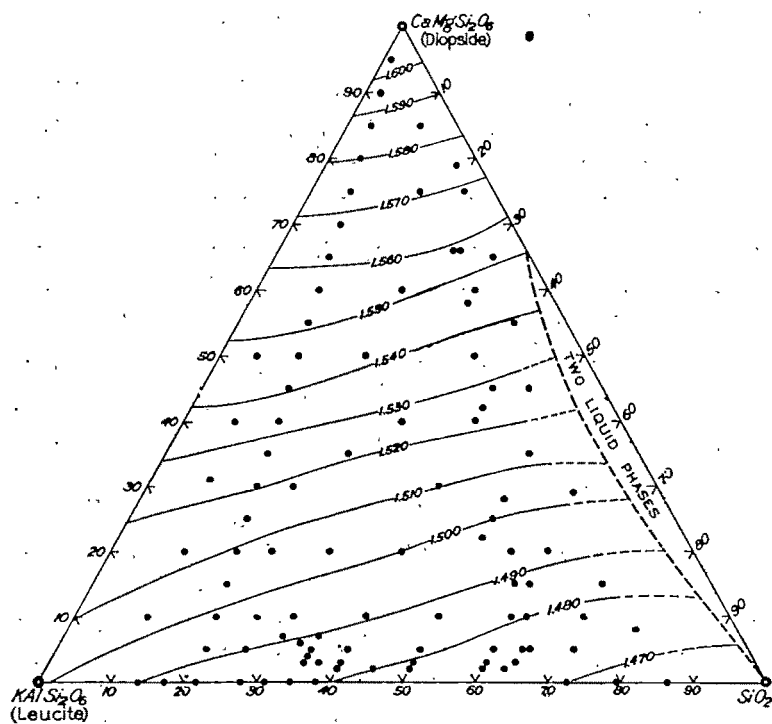


Fig. 6. Refractive indices of glasses at 25° C.

CRYSTALLIZATION OF TERNARY MIXTURES.

With perfect equilibrium, all mixtures (see Fig. 4) whose compositions lie in the triangle, leucite—potash feldspar—diopside, when completely crystalline consist of leucite, potash feldspar, and diopside. For those which lie in the field of diopside, on cooling from the completely molten state, diopside crystals appear first. When the composition of the liquid reaches the boundary curve, leucite—diopside, a second solid phase, leucite, appears. With falling temperature, leucite and diopside continue to separate with the composition of the liquid following the boundary curve, leucite—diopside, to the ternary reaction point where the temperature remains constant until all the liquid has been used up by reacting with the leucite crystals to form potash feldspar. For all compositions in the triangle, leucite—potash feldspar—diopside, all the liquid is used up at the reaction point before all the leucite has been transformed to potash feldspar by reaction with liquid. Thus the final completely crystalline product consists of the three phases leucite, potash feldspar, and diopside.

The join, potash feldspar—diopside, is a limiting case. For all mixtures whose composition lies in this join, the cooling history is similar to those in the triangle described above except that the amount of leucite crystals at the reaction point is such as to react completely with all the liquid so that leucite and liquid are exhausted simultaneously and the completely crystalline product consists of only two solid phases, potash feldspar and diopside.

All mixtures whose compositions lie in the triangle, potash feldspar—diopside—silica, with perfect equilibrium, become completely crystalline, on cooling, only at the temperature of the ternary eutectic, where they consist of potash feldspar, diopside, and tridymite. If their composition lies in the leucite field they approach the ternary eutectic along the boundary curve, leucite—diopside, or leucite—potash feldspar, to reach the ternary reaction point where *all* leucite is redissolved by reaction with liquid at constant temperature, then they follow the boundary curve, diopside—potash feldspar, to the ternary eutectic. If the composition of the mixture lies in one of the fields of silica, it approaches the ternary eutectic along the boundary curve, tridymite—diopside, or along the boundary curve, tridymite—potash feldspar. Mixtures whose compositions lie in the diopside field approach the ternary eutectic either

along the boundary curve, leucite—diopside, to the ternary reaction point and then along the boundary curve, potash feldspar—diopside, to the eutectic, or along the boundary curve, diopside—tridymite, to the eutectic. For the additional high-temperature complications of those mixtures whose compositions lie in the area of two liquid phases, the reader is referred to the excellent paper of our colleague J. W. Greig¹⁵ on immiscibility in silicate melts.

With perfect equilibrium, crystals of leucite and silica are incompatible. For a discussion of the potentialities of fractional crystallization with failure of equilibrium, the reader is referred to the paper by Bowen, Schairer, and Willems¹⁶ on the system, $\text{Na}_2\text{SiO}_3\text{—Fe}_2\text{O}_3\text{—SiO}_2$, especially pages 439-445.

PETROLOGIC CONSIDERATIONS.

In our report¹⁷ on the binary system, leucite—diopside, some attention was given to the problems of natural leucite-bearing rocks. In a short time, we expect to report on the ternary system, leucite—anorthite—silica. At that time we shall consider more fully the petrologic problems involved in the origin of leucite rocks.

We wish to emphasize here that our results on the ternary system, leucite—diopside—silica, show that for simplified rock compositions of this type, the pyroxene (diopside) is removed first, almost quantitatively, on cooling and crystallizing, leaving a low-melting liquid whose composition approaches a mixture of potash feldspar and silica (alkali-alumina silicate). One of us¹⁸ has already discussed crystal \rightleftharpoons liquid equilibrium and its bearing on the problems of rock origin by crystal fractionation, and presented a preliminary diagram for this system. For systems approaching rock compositions, residual liquids of fractional crystallization are enriched in the alkali-alumina silicates and tend to approach the low-melting region of the ternary system, $\text{NaAlSiO}_4\text{—KAlSiO}_4\text{—SiO}_2$,¹⁹ which one of us²⁰ has called petrogeny's "residua" system.

¹⁵ Greig, J. W.: *This Journal*, 13, 1-154, 1927.

¹⁶ Bowen, N. L., Schairer, J. F., and Willems, H. W. V.: *This Journal*, 20, 405-455, 1930.

¹⁷ Bowen, N. L., and Schairer, J. F.: *This Journal*, 18, 309-312, 1929.

¹⁸ Bowen, N. L.: *This Journal*, 33, 1-21, 1937.

¹⁹ Preliminary report—Schairer, J. F., and Bowen, N. L.: *Trans. Am. Geophys. Union*, 16, 325-328, 1935.

²⁰ Bowen, N. L.: *This Journal*, 33, 11, 1937.

SUMMARY.

Melting data for the system, leucite—diopside—silica are presented by means of tables and a ternary diagram. There are no ternary compounds. There are two ternary invariant points, one a reaction point and the other a ternary eutectic. The field of diopside occupies a large part of the ternary diagram, and with mixtures containing even less than two per cent diopside in their total composition, diopside appears as the primary phase. On fractional crystallization, residual liquids approach in composition a mixture of potash feldspar and silica. A diagram showing the indices of refraction of ternary glasses is given, and also a preliminary diagram for the binary system, leucite—silica.

THE GASES IN ROCKS AND SOME RELATED PROBLEMS.

E. S. SHEPHERD.

ABSTRACT.

This report had its origin as far back as 1911 when we made our first effort to determine the nature and composition of volcano gases, and the studies naturally led to the investigation of the gases in lavas and the analogous plutonic rocks.

INTRODUCTION.

When observed phenomena are not readily explained by forces whose limitations are known to us we naturally invoke other forces whose limitations are less well understood. Such explanations are of course tentative and compel a search for the limitations of the new forces invoked. Frequently these studies show that the forces postulated are insufficient to account for the observed facts and the investigation appears to lead to wholly negative results. Such negative findings are often quite useful in closing one line of speculation and turning attention to others more fruitful. Years ago geologists sought solace in the phrase "at high temperatures and pressures" and volcanologists perhaps invoke "the volatiles" of a magma as a simple and sufficient explanation of phenomena which are anything but simple. The volatiles have long been the *deus ex machina* for the many bewildering phenomena of volcanism, and the following paper is intended to supply a few, if often negative, details concerning these *dei ex machina*.

The amazing volumes of gas given off by some volcanoes, along with the vesicularity of lavas, indicate that at least some of the gases were brought to the surface by the lavas and that a study of these gases would furnish an explanation of volcanic phenomena. For over a century students have stood looking at the boiling lava in Kilauea and almost unanimously deduced that the lava was kept boiling by a continuous supply of gas from the parent magma below. It seems almost unamiable to remark that we now know that the lake is not the top of a column of liquid lava coming directly from a magma chamber below, and that the volumes of gas necessary to keep the lava molten by gas heating are too great to rise through this

hundred-meter orifice without sweeping all the lava along with it. We do not mean that gas is not a source of heat but that it is far from sufficient. Amazing rushes of gas are reported from volcanoes, for example, the great gas phase of Vesuvius,¹ but this gas the writer believes to have a somewhat different origin.

Many gas collections were made during the last century, and these were summarized by Allen,² but none of these is satisfactory from our viewpoint. It is necessary that the gas be collected from live lava in the crater uncontaminated by other gases. Experience at Kilauea, where gas may be collected directly from the molten lava, has shown us that even under these unusually favorable conditions contamination of the gases is difficult to avoid, and that gases from fumaroles, whether primary or secondary, are most interesting but bear no definable relation to the gases of the magma itself.

In an earlier paper³ we called attention to this problem of contamination. At one extreme in gas-collecting we have the collection of gases at Kilauea where it is at times possible to insert the collecting tube directly through the flame source in the molten lava of the lake. At the other extreme are gases collected as they bubbled up through meters of sea water and where one could not know which constituents of the original had been washed out by passage through water or which were added by contact of hot lava with the organic debris of the sea bottom. In between lie the fumaroles where we must take into account not only the original gases but also those resulting from contact of the hot lava with the country rock—or ash or older lavas—together with the unpredictable reactions between the hot gases and the cracks or orifices from which they issue. That such secondary or fumarolic gases may be of the greatest interest, especially when the traces of other elements are determined, has been beautifully shown by Zies,⁴ but a direct correlation with the so-called juvenile gases remains impossible and for our present purposes irrelevant; all of which is merely to

¹ Perret, F. A.: The Vesuvius eruption of 1906, Carnegie Inst. Wash. Pub. No. 339, p. 44, 1924.

² Allen, E. T.: Chemical aspects of volcanism, J. Franklin Inst., 193, 29-80, 1922.

³ Shepherd, E. S.: The analysis of gases obtained from volcanoes and rocks, J. Geol., 33, 289-370, 1925. See also Chamberlin, R. T.: The gases in rocks, Carnegie Inst. Wash. Pub. No. 106, 1908.

⁴ Zies, E. G.: The fumarolic incrustations in the Valley of Ten Thousand Smokes, Nat. Geogr. Soc., Contrib. Tech. Papers, Katmai series No. 3, 159-179, 1924.

state the obvious fact that gases which have passed through what is essentially an absorption tower (the earth's crust) can not at present give us any definite clue as to the composition of the original gases of the magma.

SELECTION AND HANDLING OF MATERIAL TO BE STUDIED.

The first difficulty which we meet is a lack of definable material. It is easy to analyze the rock or lava, though even here we must remember that the water content as determined in a chemical analysis is, as regards the rock itself, irrelevant. The chemist necessarily determines the purely arbitrary "plus" and "minus" water, but these data refer only to the powder he has prepared for analysis. It is to be regretted that more accurate data are not available, since a number of investigators have taken the figures in Washington's Tables for the water content of various rocks.

The problem of suitable vessels in which to heat the rock during evacuation was solved only when silica glass tubes became available, and these must be out-gassed before use. It is now well known that in "out-gassing" a glass, as in vacuum tubes after treatment at one temperature, if the temperature be raised above that used initially, more gas will be given off. In fact, there is no practical limit to this evolution. Only by adopting a definite procedure can one hope to duplicate one's results. The same statement applies to rocks and glasses, so the analyst must follow a definite schedule. The last traces of gas do not seriously affect the results if the same experimental conditions are followed, but without such a schedule no comparisons of the results are permissible.

Another difficulty is to find material which is definite in composition. Rock analysts usually demand that the rock be fresh and unaltered. Alteration in the sense in which we use it does not necessarily imply decomposition. To a limited extent one expects some bound water in crystalline rocks. Small amounts of water present in a magma may be completely used up to form normal hydrated minerals, as for example the micas and hornblende. But the amount which can be accounted for in this way is not large. As a maximum, assume ten per cent of mica in the rock with a water content of five per cent which at 1200° gives about 30 cc./g. In addition there will be the water present in hornblende and some adsorbed water for surfaces and cavities. As we find later, this 30 cc./g. is the average volatile content for the plutonic material studied which

we selected as free from alteration. It is evident that if there is more water it can only be present by combining with other minerals or by partially decomposing those originally present. It is this decomposition which we call alteration. It may be due to volatiles initially present in the magma, or it may be due to volatiles originating elsewhere and condensing in the rock. In the studies of rock types and relationships this demand for unaltered material is undoubtedly sound. On the other hand, in the intensive study of a rock series, the altered rocks become quite as important as the unaltered rocks, though this fact has not always been realized.

For purposes of gas study one first seeks rock showing as little alteration as possible. Later, the altered material may be even more interesting, but only when the geological relationships are being studied simultaneously. We have therefore confined our attention whenever possible to unaltered materials.

But even supposing that we can obtain fresh material—and a recently extruded lava is the only rock to which the term can apply—it is necessary that such material be handled with care. With the exception of the dense, glassy obsidians, where by chipping away the surface one can obtain the uncontaminated interior, there is always the certainty that more or less foreign matter will be present.

The vesicular lavas, and especially pumice, which have been exposed for any period will be contaminated with organic residues from various sources—bacteria, fungi, dust, and rain. One has but to heat such material and the odor betrays it. A particular case may illustrate this. In a collection of material from Little Glass Mountain, California, for which we are indebted to Professor Larsen, we found this condition:

	H ₂ O	
Dense, black glass	0.11%	No wood distillate
Type V coarsely vesiculated	0.12	A little wood distillate
Type IV more vesiculated	0.19	Appreciable wood distillate
Lightest pumice	0.36	Much wood distillate

With the exception of the dense glass, all gave the usual empyreumatic odor on heating. As these rocks had been exposed to the weather for at least a century in a rather dry climate, they furnish an excellent illustration of the adsorptive capacity of pumice.

We have mentioned care in handling; a simple example will clarify the point. Let us assume that in the collecting and

transportation of the sample the wrappings, labels, etc., deposit a centigram of cellulose on and in the specimen (very easily the case with rough vesicular lavas), and let us further assume the simplest possible dissociation of this cellulose on heating in vacuo, to give, say, 5 volumes CO, one volume CH₄, and 3 volumes H₂; then at our standard conditions (1200° C., 760 mm.) the yield will be about

CO	23.9 cc.
CH ₄	8.3 cc.
H ₂	20.1 cc.

that is, about 52 cc. of gas to be included in the total. We have grossly oversimplified the problem since these reducing gases would react with iron oxides, sulphur, and other lava constituents and seriously affect the relative quantities of fixed gases inferred. The degree to which vesiculated material can be contaminated can be appreciated only by those who have had occasion to examine such rocks. Clean material is therefore desirable, but unfortunately this ideal condition is not attainable for most rocks.

A priori one would imagine that the bubbles in a vesicular, glassy lava or pumice would be admirable places to look for fresh, uncontaminated primitive gases, and that all one needs to do is to crush the material cold in vacuo. This supposition, of course, ignores adsorption phenomena on the outside of the gas-containing vesicles. In agreement with Chamberlin's experiments, we found that no gas could be obtained in this way; the vesicles are intercommunicating.

With crystalline rocks, the case is no better. While it is true that some fine-grained rocks (certain quartzites) are relatively solid, yet there are few types which do not show one per cent or more porosity. Thus Adams and Williamson⁵ show that a pore space of one per cent is a fair average for dense rocks. Many, however, will have greater pore space, and contrary to the common notion of "solid rock," from our viewpoint it would be better to regard all holocrystalline, and especially the coarsely crystalline rocks, as appreciably shattered. This "shattering" is due to several causes; it is a natural and unavoidable condition. A crystallizing magma apparently concentrates its volatiles in the liquid portion, which means that near the end the concentration of volatiles in the last liquid may

⁵ Adams, L. H., and Williamson, E. D.: The compressibility of rocks and minerals at high pressures, J. Franklin Inst., 195, 512, 1923.

be very high even though the total volatile content of the magma was low. The spine of Mt. Pelée and the boulders carried by the nuées ardentes illustrate this point. These lava blocks are of a sugary texture—almost as if every crystal was separated from every other. In this case we know that some of the interstitial lava was highly charged, even to the explosion point; the remaining blocks left by a nuée were apparently less charged but enough so to be extremely porous. We may suppose that however free the passages for escape may have been, there will always be room for a thin film of the gas phase between many of the crystals, whatever the pressure may be. The crystals always include a small amount of water and may even include vesicles containing water and at times CO_2 . The result is that rocks contain an infinite number of minute cavities and surfaces for adsorption effects. Quite as important in producing and maintaining porosity is the differing thermal expansion of crystals not only of one mineral compared to another but with differing axes of the same crystal. The constant shifting of the geotherms with time, the changing pressures with isostatic readjustments, loading and unloading, and the daily warping of the earth's crust by tidal stresses⁹ keep the crystals in a continuous if minute state of movement.

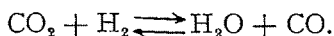
There must be a usually slow but continuous movement of gases or vapors through the rocks, partly induced by these minute but definite shifting movements, therefore one can not believe that we shall ever be certain that the gases obtained from even the best holocrystalline rocks will bear any definite relation to those initially present. We can not know how much of the alteration observed in a rock is due to reaction with its initial volatiles and how much is due to foreign volatiles which have contaminated the mass in later periods.

This uncertainty is accentuated when some of the characteristics of gas reactions are considered. The determination of gas equilibria is one of the tantalizing jobs which chemists encounter; not only are the reactions themselves subject to complications, but they are also seriously affected by the walls of the containing vessel. Adsorption phenomena together with catalytic effects, as of the iron oxides altered by small amounts of other metals, enter in. Then, too, the reactions shift with temperature, pressure, the relative proportions of the gases entering into the reaction or diluting the mixture, and also with

⁹ There should be an appreciable heat effect involved in earth tides, though no one seems to have tried to evaluate it.

the rate of removal of one or more reaction products from the field of action. It is clear that even if we had imprisoned in the rock the "warranted genuine" magmatic gases, the effort to extract them, involving as it does changes of temperature and pressure, along with the uncertainties as to the length of time the mixture remains in contact with catalytic surfaces, defeats any attempt to interpret the analytical data in terms of the original composition of the gases in the cooling magma.

For those who may not have considered this aspect of the problem we may list a few of the reactions involved. First and foremost is the "water gas" equation



This classic equation has been intensively studied and the effect of concentration, temperature, and pressure definitely established for a limited range of conditions. But the results can not be applied to our problem because of extraneous factors introduced by the varying composition of the rocks themselves. We know what happens under carefully predetermined conditions, but in nature we find the gases of this equation contaminated by sulphur, halogens, silicon, iron, copper, zinc, lead, nickel, chromium, molybdenum, vanadium, etc., ad infinitum, some acting as catalysts, others poisoning the catalysts, and the whole chaotic mess enclosed by and enclosing the unpredictable pore spaces with unpredictable surfaces. In other words, we are not yet able to make any use of this equation without straining our present data inexcusably.

Reactions between mixtures of the following elements will be present: H_2 , O_2 , S_2 , Cl_2 , F_2 , and Si, in greater or lesser degree.⁷ Perhaps the only gas reactions which have not been

⁷ Many gas reactions have been suggested in a search for energy sources for volcanoes. Most of these are based upon the tables for heat of formation which tables are far from satisfactory for the purpose since the whole hypothesis is an extrapolation with very scanty experimental checks. Thus there has appeared from time to time the dissociation of water into hydrogen and oxygen at high temperatures, the gases then being recombined later to produce the desired heat. According to our present knowledge this dissociation, if appreciable in amount, involves temperatures far above 2000° C. and therefore belongs, if anywhere, in a region far removed from any with which we have to deal. Another suggestion is to use ferrous oxide to react with water, thus giving ferric oxides and hydrogen. The hydrogen so obtained is then to be used to reduce the ferric oxides to ferrous, furnishing heat. Quite aside from the problem of moving the gases about and having them react at the precise spot needed and without loss of energy, there remains the regrettable fact that we are not dealing with ferrous oxide but instead with ferrous silicates, in which case the sign of the heat change is reversed.

exploited heretofore are those involving Si, S₂, and H₂. We elsewhere pointed out that SiH₄ is a probable constituent of magmatic gases at the higher temperatures. Any place where free hydrogen and a silicate are in contact at temperatures around 1100° will show some SiH₄ formation. Of even greater significance are the silicon sulphides which Hempel believed he has shown to be present in Vesuvian lava.⁸ These sulphides form with great ease whenever sulphur and silica are heated to about 1100° under reducing conditions; the reaction is a commercial one used in the purification of bauxite. At some depth, therefore, silicon sulphide may be expected

Then, too, if all the iron in our richest iron-bearing lavas could be induced to obey our will there would remain the fact that the heat so obtainable would have to be distributed through the remaining ninety per cent of the rock and could at best raise the temperature only a few degrees. With the andesites and rhyolites the heat available from this source approaches zero. These reactions should not be invoked.

Of the purely gaseous reaction between CO₂, H₂O, and S₂, shifting equilibria can furnish heat if we are allowed to run the reaction just as we please and where we please. But before one indulges in such speculation one should also arrange to move the tremendous quantities of gas about and also compute the quantities needed. The results of this arithmetic are sure to be discouraging. Such gas reactions are no doubt a factor in supplying energy, but a very minor factor, and none of those suggested bears any relation to the average composition of volcano gases as we might expect it to do were it a dominant factor.

There is no limit to the arithmetic which can be expended in an effort to secure volcanic energy. As an example of this sort we shall consider one mode, that is, simple heating by hot gases. Approximations as to the heat loss at Kilauea using various reasonable assumptions give the order of magnitude around 400,000,000 calories per second as a conservative estimate. We shall assume all the gas to be water vapor with a specific heat of 0.5. One gram of steam at 1200°, 760 mm. has a volume of about 6.77 liters. Assume further a temperature drop of 300° in the gas, say 1400 to 1100°. Then for every 6.77 liters of gas evolved there would be available 150 calories. To supply the 4,000,000 calories we should need 2,666,600 grams or 18,040,000 liters per second, that is, 18,040 cubic meters per second. Assume a circular lake 100 meters in diameter. Then 18,040 cubic meters corresponds to a cylinder of gas 100 meters in diameter and 2.3 meters high. Therefore the gas would have to issue at such a rate as to pass this 2.3 meter cylinder each second, or in terms of wind velocity, about five miles an hour. As a matter of fact the lake is always largely covered with floating crusts so that the available free surface of fresh lave is more nearly a hundredth part of the assumed area, which would raise the required rate of gas evolution accordingly. To reduce these figures to every-day experience one need only consider the rate at which a pan of water must boil in order to furnish a steam jet of its own diameter issuing at the rate of seven feet per second. Transfer this concept to the more viscous lava, say more viscous than hot porridge, and one sees the impossibility of any such rate of gas evolution from the crater. This does not preclude intense gas blasts from suitable openings but does exclude gas heating as the main factor at Kilauea.

⁸ Hempel and Haasy: Z. anorg. Chem., 23, 32, 1904; Dolch, P.: Chem. Fabrik, pp. 512-514, 1935.

and a slow but continuous removal of silicon from depth toward the surface may be expected to have been under way from the beginning. While we are not used to considering silicon compounds as "volatiles," they evidently must be so treated. Silicon halides are also formed and hydrolyzed readily. Thus we have not only SiF_4 easily formed at high temperatures but also the fluosilicic acid H_2SiF_6 quite stable in acid solutions and volatile with steam. Furthermore, the fluosilicates, most of which are quite soluble, add their mite to the chemist's confusion when he considers the various possible solutions with which rocks are contaminated. In addition to the unexpected volatility of the compounds is the stability of colloidal silica solutions, so that this element which the chemist regards as inert and insoluble is really surprisingly mobile.

The above considerations show that the gases which we find in the crystalline rocks are too indefinite in origin to answer the questions asked in the problem as originally stated. Neither the amount nor relative compositions tell anything definite about the "juvenile gases."

Even though we can not hope to learn much about the magmatic gases from our data, yet these same data will yield information that will be useful in studying the rôle of the gases in later stages of the igneous activity. After all, the phenomena with which we are concerned are much nearer the surface of the earth than the primitive magma. Thus it is important to know what gaseous elements, and the total amounts thereof, can be set free on reworking or reheating rock in nature, for with these gases we have to deal. For this purpose it seemed wise to determine at least the minimal amounts of gas which might be expected, letting the state of combination be what it might. We do not know what may have been the distribution of the gaseous constituents of, say, a granite magma, but we can know what gases and volumes will be given off when a particular granite is reheated. We have therefore examined a number of lavas and the corresponding plutonics to see what volatiles were available in the various transformations to which rocks are subjected in the crust. We selected material showing a minimum of alteration of whatever kind and compared this with such lavas and volcano gases as were available. The reason for selecting material that showed a minimum of alteration was similar to that which made earlier investigators omit water from their determinations. Since they were unable to say how much of the water belonged properly to the rock and

how much was adventitious, they excluded all of it. In our work it developed that the water must be included, though alteration in a rock introduces an indefinite quantity of total volatiles. However, if we are not concerned as to the primitive magmatic volatiles but are interested instead in the volatiles available for surface and near-surface phenomena, then water of whatever origin becomes of first importance.

VOLCANO GASES.

It will be better, perhaps, if we begin our examination of the gases with a review of the work on volcano gases.

Our first interest in volcano exhalations was aroused by observations made at Kilauea. The analyses of these gases were published long ago,⁹ but they will be reprinted here (Table I) in order to compare the gases obtained from the active lava with those obtained by "out-gassing" the same lavas in vacuo. The Hawaiian gas analyses were made on samples collected in vacuum tubes. All the samples were obtained at Kilauea with the exception of ML 1 and 2 which were collected by Dr. T. A. Jaggar from a Mauna Loa eruption. The analyses listed with a J are that splendid series of tubes collected for us by Doctor Jaggar in 1919. By carefully choosing the time and place of collection, using both his knowledge of the crater activity and a very real courage, Doctor Jaggar has given us here what is unquestionably the most satisfying, indeed the only satisfying collection of volcano gases that has ever been made. To him we are deeply indebted for what may be characterized as the crucial test of the Kilauea gases. The S series was collected by Shepherd in 1917 and was taken from the most favorable sources available. The tubes were, however, more frequently contaminated with air, owing to less favorable sources than those of the J series.

The one obvious fact brought out by the analyses shown in Table I is the lack of any definite relationships among the constituents involved. As is well known, Kilauea remains active over long periods and one would therefore infer that foreign volatiles would long since have been swept away. When these collections were made, the lake had been active for many years. Surely here, if anywhere, we might expect some sort of equi-

⁹ Shepherd, E. S.: Bull. Hawaiian Volcano Obs., 9, 83-88, 1921. Day, Arthur L., and Shepherd, E. S.: Water and volcanic activity, Bull. Geol. Soc. Am., 24, 573, 1913.

TABLE I.

Volume percentages at 1200°, 760 mm., for Kilauea gases from vacuum tubes.

Number	CO ₂	CO	H ₂	N ₂	A	SO ₂	S ₂	SO ₃	Cl ₂	H ₂ O
J 2	5.79	0.00	0.00	7.92	udt	4.76	0.00	2.41	4.08	75.09
J 3	6.63	0.22	0.15	2.37	0.56	3.23	0.00	5.51	1.11	80.31
J 4	6.79	0.14	0.17	2.33	0.00	1.38	0.15	3.43	0.62	84.98
J 6	0.87	0.16	0.07	20.01	0.00	0.01	0.00	0.13	0.03	78.71
J 8	47.68	1.46	0.48	2.41	0.14	11.15	0.04	0.42	0.04	36.18
J 10	16.44	0.11	0.10	15.03	0.21	13.57	0.05	3.56	0.03	50.88
J 11	20.93	0.59	0.32	4.13	0.31	11.42	0.25	0.55	0.00	61.56
J 12	1.42	0.05	0.08	0.68	0.05	0.51	0.07	0.00	0.03	97.09
J 13	16.96	0.58	0.96	3.35	0.66	7.91	0.09	2.46	0.10	67.52
J 14	14.81	0.47	0.17	2.91	0.00	3.65	0.10	1.03	0.00	76.84
J 15	11.53	0.13	0.10	6.20	0.16	6.14	0.03	1.70	0.10	73.89
J 16	18.03	0.56	0.67	3.11	0.08	8.53	0.15	2.53	0.08	66.25
J 17	11.61	0.37	0.58	1.29	0.04	6.48	0.24	0.00	0.05	79.31
J 18	17.55	0.74	0.83	4.50	0.12	10.81	0.22	3.22	0.13	61.88
S 1	2.65	1.04	4.22	23.22	udt	0.16	0.70		udt	67.99
S 2	17.95	0.36	1.25	37.84	udt	3.51	0.49		udt	38.48
S 3	33.48	1.42	1.56	12.88	0.45	29.83	1.79		0.17	17.97
S 4	11.12	3.92	1.42	0.51	8.61		0.02	77.50
S 5	9.54	1.12	1.53	10.47	0.00	9.90	2.72		0.00	64.71
S 6	1.97	0.82	0.21	3.50	0.07	0.95	2.70		0.00	89.77
S 7	17.25	0.62	0.76	5.88	0.18	9.75	1.07		0.25	64.18
S 8	15.27	0.45	0.70	0.87	0.14	6.98	0.49		0.00	75.08
S 9	8.32	0.82	1.82	8.92	0.29	16.80	2.48		1.01	59.97
S 10	1.54	0.43	0.37	2.44	0.39	0.00	3.56		1.34	89.93
ML 1	3.84	0.03	0.00	15.80	0.58	1.22	0.00	2.08	0.00	75.44
ML 2	6.42	0.19	0.01	15.39	0.42	1.95	0.00	8.12	0.00	67.43

librium and here we surely should be able to collect the true juvenile, that is, magmatic gases. Nothing of the sort appears in the data, and while one of the factors in furnishing heat may very well be the heat resulting from the shifting equilibria of the gases involved, as suggested by Day,¹⁰ this must be a minor factor in view of the quantities of gas involved in comparison with the heat losses and specific heat of the lava itself. Any effort to compute such heat effects is vitiated by the absence of data as to the total volume of gases per unit of time, and even more so by our inability to handle theoretically mixtures of such complexity and subjected to such indeterminable conditions. It is clear that the "water gas" reaction is involved, with the equilibrium well over toward the water side. All the gases are well oxidized, and though enough sulphur is usually present to give occasional flames, the absence of any quantity of free

* Day, Arthur L.: Some causes of volcanic activity, Franklin Institute, 24 pp., 1925. Also J. Franklin Inst., 200, 161-182, 1925.

hydrogen is shown by the absence of explosions when great bubbles of gas (as in the fountains) break out from the surface.

Of much less importance, but perhaps significant, is the content of rare gases. These we have listed as argon. A large part of this may properly be attributed to admixed air. This contamination may occur in filling the vacuum tube and can be partly corrected if the analysis shows free oxygen. This correction, however, is obviously far from perfect. We may also expect that the air carried down by sinking crusts at Kilauea will account for a further unpredictable amount.¹¹ Some argon might be supposed to enter the lava at still greater depths since the lava has to work its way up through a brecciated, and therefore adsorptive, mass of old lava. But there is no intelligible relation between the figures for argon and nitrogen. We have often tested for helium in the course of our analyses and with negative results. It may be present but certainly in no significant amount. If, as some maintain, the energy of volcanoes derives in part from radioactivity, one might hope that volcano gases would show at least appreciable quantities of helium, but neither in the rocks from Kilauea nor in other rocks and lavas examined is the total of rare gases significant.¹² Nitrogen is believed to come partly from nitrides. Gautier, the most critical student in this field, made a number of interesting tests which satisfied him that the rocks studied contained iron nitride which would account for traces of NH_3 commonly appearing in accounts of volcano gases. One can not accept this conclusion without reserve. Experiments made upon fresh, carefully handled basalt might be more conclusive, but no such tests have been made. It is not probable that any nitride could withstand the age-long soaking in water which the plutonics have endured, nor could one distinguish between NH_3 derived from this source and NH_3 of meteoric origin. The presence of nitrides or NH_4Cl in fumaroles together with the rarer elements needs much more study before one would feel any confidence that it originated in the juvenile gases, and this remains true even though we grant that at some depth in the earth nitrides ought to be stable and common.

The explanation of the lack of any uniformity of com-

¹¹ Jaggar developed his "surface combustion" hypothesis on the assumption that the sinking crusts would carry down enough oxygen to burn combustible gases. The great excess of nitrogen which combustion by trapped air implies is not borne out by the analyses of the gases.

¹² For example, there are helium-bearing strata in Southeastern Utah (the San Rafael swell) but our No. 29, the Marvine laccolite in the Henry Mountains, shows no abnormal rare gas content.

position in these Kilauea gases appears from the following observations. Most fountains burst without any visible flame, whatever the "seeing." Then a fountain breaks, emitting a purplish-brown vapor apparently almost pure sulphur vapor. One sees fumed wall rock (highly impregnated with sulphur) avalanche into the lake with great boiling and spattering as the condensed volatiles are revolatilized. Other blocks may slip into the lake with little or no disturbance. It is a fair inference that the variable streaming of the lava, the chilled lava crusts which instantly coat sinking blocks and the irregularly sinking crusts (for the lava lake is barely above its freezing temperature), and the shallow character of the lake itself all tend toward a most irregular mixing of whatever gases may be present.

The older conception of the lake, which in 1912 we fully shared, wherein the lake was thought to be merely the top of a column of molten magma, the column going down directly to the hypothetical magma reservoir below, would have implied a rather efficient mixing of gases and hence some sort of uniformity. The absence of any such uniformity of composition is quite in accord with those physical features of the lake which Doctor Jaggar's long series of observations and tests has established.

Jaggar's remarkable sounding-experiments and observation of the lake at times when a sudden drop of lava level exposed the bottom, the input, and the drainage openings, give us a wholly different picture.

To the writer it now seems clear that the lava lake is not the top of a column of liquid lava but that it is a lava spring with subterranean drainage. The actual lake is a shallow pool poised on top of a breccia through which several small streams of lava work their way to the surface, the original lava coming probably from under Mauna Kea or Mauna Loa and thence drained off, for the most part, under the sea. Frequently it breaks out along the line of the pit craters or out on the Kau desert.

Jaggar¹⁴ has shown that at times of subsidence a tremendous volume of talus avalanches into the heart of the mountain. This talus acts as a condenser for the fumes of the receding lava. With a renewal of activity the new lava must work its way up through this old talus, in doing which the condensed fumes are once more set moving to contaminate whatever gases the new lava may bring with it.

¹⁴ Bull. Hawaiian Volcano Obs., 12, No. 12, 1924.

To those who have not followed the record of Kilauea's eruptions, this concept may seem fantastic. To all such we commend the record both of outbursts in the Kau region and particularly Father Coan's description of the 1840 Kilauea flow.¹⁶ The difficulty some have in understanding these craters lies in a preoccupation with the over-simplified textbook diagrams. There are great differences between a basaltic edifice resting on basaltic flows and a volcano of more viscous lava resting on or penetrating a sedimentary or solid igneous platform.¹⁶ In the case of Hawaii, the volcano is a pile of loose flows and tubes, or tiles. It is an extremely porous mass without the coherence of our continental edifices. Not only that, but the flows are never welded together.¹⁷ Typical pahoehoe lava has a density of about 2.0 whereas the specific gravity is about 3.0. The macro-porosity is well shown in Goranson's computations,¹⁸ according to which the mountains, above sea level, at least, have a density (as determined by gravity measurements) of between 2.1 and 2.8. This means that many lava channels must be present.

These channels can produce changes in the composition of the gases issuing from the lava. If one channel is blocked, the lava seeks a new outlet. This phenomenon is readily observed in watching both the rising and the sinking pools at the edges of the lake. But in changing channels the lava passes through fumed areas in which both magmatic gases and drainage from above have been active. One result will be a sudden increase in the total sulphur content because sulphur is one of the most easily condensed of the common volatiles present. Consider this action to be going on in the breccia underneath the lake, and we see why no constancy of composition is to be expected.

¹⁶ Brigham, W. T.: The volcanoes of Kilauea and Mauna Loa, on the island of Hawaii, their variously recorded history to the present time, Bishop Museum Press, Honolulu, p. 50, 1909.

¹⁶ Consider Vesuvius, where the lava works its way up through several thousand feet of limestone and pieces of more or less altered limestone are erupted; or Mt. Pelée and Lassen Peak, where the lava is so viscous that it reaches the crater as domes and spines, and a free-flowing lava—a good lava flow—is rare.

¹⁷ The record of the outbreak of Hawaiian lava flows is consistently the same; lava wells up in the crater, building up pressure of the lava column until at some point a pathway through the mountain opens, then the surface flow begins, not from the crater but out of some point on the mountain's flanks. This is the regular course of eruption for Mauna Loa and even with the more accessible subterranean-submarine exits which we assign to Kilauea, breaks through the side toward the pit craters (the pit craters are on the side of the mountain toward the sea) or in the Kau desert are not infrequent.

¹⁸ Goranson, R. W.: This Journal, 16, 117, 1928.

GASES FROM LAVAS.

It seemed reasonable that if we could pump the residual gases out of the freshly collected Hawaiian lava it might be of interest to compare it with the gases which the lava gave off as collected in vacuum tubes at the volcano. The results of this study are given in Table II. Obviously, Tables I and II could be interchanged without difficulty. There is no more constancy in one than in the other. The residual gases of the lava are the same and as variable as the gases of the vacuum tubes. The hydrogen averages a little higher and the nitrogen lower, but we feel justified in assuming that extracting the gases from fresh lava by heating in vacuo will tell us just as much about the gases of an eruption as will vacuum tubes. The only additional information would be that of the fumaroles and incrustations, which in carefully handled cases (Zies' paper on the incrustations at Katmai is a beautiful example) is likely to be even more instructive now that the general character of the main gas content is established.

We next examined a series of six other types of lava. In Table II, with descriptions in Table III, we have assembled the entire series, both lavas and the analogous plutonic rocks.

In the first section are given the results for obsidians; in the second group, the andesites from Mt. Pelée, Martinique, and Lassen Peak, California; then the basalts of Kilauea and Mauna Loa; and finally typical plutonics. These last are: granite from Stone Mountain, Georgia; the Barre and North Jay granites from Vermont; a selected specimen from the Henry Mountains, Utah (Marvine laccolite); the Maryland diabase from near New Market, Maryland; and the diabase from Granton, New Jersey. About the only tendencies visible in the tables are the dominance of H_2O and a clustering of the total cc./g. around 5 or 6 for lavas. The few exceptions such as Numbers 2, 5, and 6 of the obsidians; 11 and 14 of the andesites are readily accounted for by the nature of the specimens, as described in Table III, and in a succeeding discussion.

In the selected plutonics examined, the tendency is for the total volatiles to cluster around 30 cc./g. (approximately). This figure of course may become much greater if alteration is present. The Barre granite contains visible calcite of whatever origin, and it was the threefold increase in total volatiles from the Granton diabase that first called our attention to the fact that the rock was altered. The earlier examination had over-

TABLE II.
Gases from rocks in vacuo.

Lava Numbers*	CO ₂	CO	H ₂	N ₂	A	S ₂	Cl ₂	F ₂	H ₂ O	cc./g
Obsidians (Rhyolitic)										
(1) 1	1.402	0.705	0.101	2.897	0.000	0.367	2.965	3.163	88.386	1.19
(2) 2	1.595	0.035	0.174	1.420	0.000	0.014	0.499	0.516	96.299	27.10
(3) 3	0.179	0.073	0.501	3.897	0.002	0.000	1.820	7.795	89.246	1.41
(4) 4	0.075	0.008	2.253	1.153	0.000	0.039	1.498	2.205	94.434	4.86
(5) 5	0.672	0.007	0.377	0.138	tr	0.000	1.713	4.329	92.761	55.3
(6) 6	0.077	0.032	0.080	0.053	udt	0.000	0.069	1.136	98.551	214.8
Andesitic Lavas										
(7) MP/4	8.609	1.473	0.199	1.228	udt	1.732	0.934	2.575	83.248	7.1
(8) MP/5	10.109	2.007	0.252	0.854	0.008	0.422	0.387	3.317	82.525	4.8
(9) MP/6	20.260	1.391	0.185	2.494	0.023	1.908	1.575	1.420	70.726	4.3
(10) MP/1	7.441	1.256	0.435	2.371	0.007	2.892	10.495	4.289	70.812	5.9
(11) MP/7	0.824	0.214	0.427	0.213	tr	0.053	0.991	1.038	96.227	26.5
(12) LP	2.070	0.623	0.412	0.577	0.003	0.882	0.297	1.524	93.658	9.5
(13) LP	1.187	0.310	0.210	0.116	0.018	0.215	0.428	nd	97.519	7.8
(14) LP	1.959	0.503	1.187	0.029	0.0003	0.123	0.129	nd	96.067	10.6
Basaltic Lavas										
(15) P 1911	5.673	0.601	1.085	0.269	0.003	1.384	0.404	udt	90.580	5.4
(16) P 1919a	11.757	0.148	0.376	0.280	tr	1.662	1.334	3.609	80.834	6.9
(17) P 1919b	11.172	0.045	0.464	1.305	tr	1.674	1.030	6.203	78.100	7.3
(18) KMP 1923	6.262	0.038	0.435	2.047	0.003	0.988	1.152	14.115	74.953	5.0
(19) KMA 1923	7.893	1.877	0.520	2.564	0.005	0.454	0.544	11.733	74.402	4.2
(20) KAA	6.80	3.83	6.18	1.31	0.01	0.72	0.26	udt	80.17	9.8
(21) K 1924	9.337	0.026	0.382	2.109	0.042	1.094	0.127	5.218	81.663	0.69
(22) KJ 1917	2.339	0.069	3.131	2.516	0.002	1.957	0.739	13.331	75.914	6.6
(23) Loa 1926	15.304	1.426	4.410	5.193	0.015	0.236	0.213	0.000	73.199	6.2
(24) ML 3a	12.982	0.985	3.872	1.749	0.037	0.475	0.055	0.000	79.892	2.9
(25) Niuafooua	10.358	8.276	1.108	7.207	0.018	1.278	0.430	0.000	71.322	3.9
Plutonic Rocks										
(26) Stone Mt. Granite	1.965	0.081	4.823	0.334	0.007	0.268	0.007	1.970	90.512	34.2
(27) N. Jay Granite	4.236	0.536	11.603	1.228	0.024	0.159	0.051	2.563	79.599	29.4
(28) Barré Granite	19.634	2.215	5.502	2.190	0.025	0.724	0.180	0.254	69.276	57.3
(29) Marvinne Laccolite	9.463	0.814	13.455	0.566	0.002	4.042	0.300	1.914	69.439	31.2
(30) Maryland Diabase	0.894	0.023	4.813	1.911	tr	1.844	0.189	0.275	90.059	30.0
(31) Granton Diabase	2.425	0.026	2.944	0.797	0.000	0.079	0.986	0.341	92.399	89.9

*The numbers in parentheses in the first column are serial cross-reference numbers for Tables II and III. In the second column is listed the name or symbol that identifies a particular rock.

Computing these analyses to the third decimal is made necessary by the method and composition. In analyzing the gas, water is determined gravimetrically and this large volume added to the analysis of the fixed gases. These may vary anywhere from one to fifteen cc. and no extraordinary precision can be claimed for them; if small but definite quantities of the fixed gases are to appear in the final computation the figures must be carried past the one-tenth cc. limit as usually computed.

NOTE FOR TABLES II AND III.

In the analysis of gases collected in vacuum tubes it is often feasible to separate the sulphur gases into free sulphur and its oxides. This separation illustrates the inherent difficulty in such analyses. The gases are not in equilibrium even as collected. We find, then, a mixture of SO_2 , SO_3 , with free sulphur and in exceptional cases H_2S . In such a mixture on standing, for example during the interval between collection and analysis, rearrangements are certain to take place. Hence, the figures represent merely what was present at the time of analysis. With gases extracted from lavas in vacuo, this separation is more difficult and often out of the question, so that as work progressed we tended more and more to state all sulphur as S_2 because its distribution in the possible combinations would be fortuitous. Similarly, fluorine is not to be determined in vacuum-tube collections, though nowadays the determination is possible for lavas or for gases pumped from the lavas. With these exceptions Tables I and II can be compared directly.

It may be repeated here that the gases obtained from out-gassing lavas and rocks represent the volatiles which can be obtained from the material under our conditions. No method of attack will deliver all the volatiles in one operation.

TABLE III.

Rock Analyses.

Lavas—Big Glass Mountain, California.

Ser. No.*	1 (1)	2 (2)	#19103	Type C
SiO_2	73.34	73.38	73.59	72.64
Al_2O_3	13.35	13.69	13.78	14.07
Fe_2O_3	0.58	1.84	0.60	0.77
FeO	1.27	0.13	1.30	1.45
MgO	0.37	0.37	0.33	0.49
CaO	1.41	1.38	1.39	1.60
Na_2O	4.13	3.92	4.19	4.25
K_2O	4.45	4.22	4.32	4.08
H_2O^+	0.33	0.34	0.14	0.11
H_2O^-	0.03	0.05
CO_2
TiO_2	0.30	0.28	0.27	0.36
ZrO_2	0.01	tr
P_2O_5	0.18	0.08	0.12	0.11
SO_2
Cl	0.08	0.12
F
S	0.10	0.03
Cr_2O_3
V_2O_5
MnO	0.02	0.02	0.02	0.02
NiO
BaO
SrO
Li_2O	p.n.d.
Cu

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavas—Little Glass Mountain, California.

	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6
SiO ₂	73.59	73.34	73.22	73.47	73.46	73.49
Al ₂ O ₃	14.03	13.96	13.65	13.72	13.72	13.65
Fe ₂ O ₃	0.42	0.51	0.40	0.61	0.46	0.60
FeO	1.43	1.31	1.41	1.24	1.27	1.29
MgO	0.36	0.36	0.21	0.37	0.41	0.40
CaO	1.38	1.53	1.38	1.38	1.57	1.40
Na ₂ O	4.04	4.22	4.23	4.21	4.21	4.17
K ₂ O	4.34	4.35	4.30	4.27	4.30	4.27
H ₂ O+	0.12	0.10	0.39	0.34	0.33	0.31
H ₂ O—	0.06	0.07	0.16	0.12
CO ₂
TiO ₂	0.31	(0.36)	0.29	0.28	0.28	0.31
ZrO ₂
P ₂ O ₅	0.09	0.13	0.11	0.22	0.13	0.14
SO ₃
Cl	0.03	0.09
F	0.03
S	0.02	0.05	0.02	0.04	0.03	0.03
Cr ₂ O ₃
V ₂ O ₅
MnO	0.02	0.03	0.03	0.02	0.02	0.03
NiO
BaO
SrO
Li ₂ O	p.n.d.
Cu

TABLE III—Continued.

Ser. No.*	Lavas—		Mt. Mor- rison		Newberry Volcano,		Cerro Noagua, N. Mex.		Obsidian Cliff Yellow- stone
	Coso Mts., Calif.		Mono Craters	Quad- rangle	Oreg.				
	Type 1 (3)	Type 2 (4)			No.75	Black Obsidian (5)	Pitch- stone (6)		
SiO ₂	76.09	75.92	76.13	76.27	73.40	76.35	73.14	76.78	
Al ₂ O ₃	12.60	12.31	12.49	12.24	13.98	12.34	13.41	12.09	
Fe ₂ O ₃	0.49	0.40	0.36	0.50	0.24	0.47	0.33	0.56	
FeO	0.85	0.68	0.72	0.76	1.76	0.60	0.20	0.81	
MgO	0.14	0.08	0.02	0.02	0.18	0.03	0.08	0.10	
CaO	0.58	0.59	0.54	0.60	1.35	0.38	0.58	0.57	
Na ₂ O	4.03	4.26	4.68	4.90	4.15	4.29	4.28	3.79	
K ₂ O	4.43	4.36	4.72	4.49	4.10	4.39	4.31	4.93	
H ₂ O+	0.26	0.98	0.20	0.15	0.40	0.91	3.10	0.12	
H ₂ O—	0.06	0.09	0.06	0.10	0.00	0.12	0.08	
CO ₂	
TiO ₂	0.09	0.06	0.08	0.10	0.20	0.09	0.06	0.08	
ZrO ₂	0.01	0.00	0.00	tr	tr	0.01	
P ₂ O ₅	0.06	0.15	0.02	0.04	tr	0.02	0.01	0.09	
SO ₂	
Cl	0.08	0.06	0.13	0.11	0.06	0.08	0.05	
F	0.13	0.14	0.07	0.06	0.06	0.08	0.15	0.15	
S	0.00	0.00	0.01	tr	0.01	0.00	0.06	
Cr ₂ O ₃	
V ₂ O ₅	
MnO	0.02	0.02	0.02	0.01	0.06	0.14	0.02	
NiO	
BaO	0.00	0.00	tr	tr	0.00	
SrO	
Li ₂ O	p.n.d.	
Cu	

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Ser. No.*	Granites			Marvine Laccolite
	Stone Mt., Ga. (26)	Barre, Vt. (28)	N. Jay, Vt. (27)	H. (29)
SiO ₂	73.39	70.48	73.41	63.73
Al ₂ O ₃	14.41	14.42	14.17	17.71
Fe ₂ O ₃	0.09	0.63	0.22	2.09
FeO	0.70	1.59	1.19	2.15
MgO	0.27	0.89	0.19	1.16
CaO	1.05	1.68	1.02	5.69
Na ₂ O	3.96	3.98	3.33	4.56
K ₂ O	5.07	4.48	5.35	1.76
H ₂ O+	0.39	0.43	0.31	0.34
H ₂ O—	0.05	0.05	0.02	0.05
CO ₂	0.54	p.n.d.
TiO ₂	0.27	0.44	0.19	0.45
ZrO ₂	tr	0.01	0.02	0.03
P ₂ O ₅	0.57	0.31	0.12	0.25
SO ₂
Cl	0.03	0.02	0.04	0.02
F	0.04	0.06
S	0.02	0.03	0.01	0.02
Cr ₂ O ₃
V ₂ O ₅
MnO	0.03	0.02
NiO
BaO	0.02
SrO
Li ₂ O
Cu

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavasa—Lassen Peak.

	LP 32	LP 18	LP 2	LP 34	LP 7	BH 1
SiO ₂	70.17	67.98	66.06	65.56	64.80	64.53
Al ₂ O ₃	14.98	15.69	15.93	15.41	16.26	16.60
Fe ₂ O ₃	0.87	2.93	1.53	2.38	1.11	1.76
FeO	1.78	0.42	2.36	2.16	3.17	2.34
MgO	1.28	1.47	2.15	2.37	2.39	2.55
CaO	3.16	3.86	4.53	4.92	4.83	5.18
Na ₂ O	4.49	4.42	4.18	3.51	4.13	3.87
K ₂ O	2.74	2.33	2.28	2.35	2.13	2.09
H ₂ O+	0.35	0.20	0.16	0.34	0.09	0.23
H ₂ O—	0.02	0.11	0.11	0.15	0.16
CO ₂
TiO ₂	0.39	0.45	0.55	0.48	0.53	0.61
ZrO ₂	0.05	0.03	0.03	0.01	0.03
P ₂ O ₅	0.25	0.15	0.19	0.19	0.26	0.25
SO ₂
Cl
F
S	0.01	0.01	0.01	0.02
Cr ₂ O ₃
V ₂ O ₅
MnO	0.03	0.07	0.08	0.07	0.08	0.07
NiO
BaO	0.03	0.05	0.01
SrO	(0.01)	(0.06)	(0.07)	(0.03)	(0.02)
Li ₂ O	(0.02)	(0.01)	(0.01)	(0.01)	(0.02)
Cu

TABLE III—Continued.

Lavas—Lassen Peak.

	LP 10	LP 28	BH 3	CC 6	LP 21	CC 7b
SiO ₂	64.49	63.45	60.55	59.76	58.77	57.54
Al ₂ O ₃	16.33	17.20	16.90	16.96	18.16	17.86
Fe ₂ O ₃	2.55	1.80	1.95	2.31	3.02	2.81
FeO	1.85	2.42	3.12	3.18	2.92	3.45
MgO	2.65	2.62	3.14	3.80	4.35	3.67
CaO	5.04	5.28	5.89	6.71	7.30	7.29
Na ₂ O	4.38	4.13	3.42	4.20	2.97	4.04
K ₂ O	2.13	1.65	2.02	2.16	1.19	1.65
H ₂ O+	0.08	0.83	1.30	0.15	0.10	0.13
H ₂ O—	0.01	0.32	0.27	0.08	0.02	0.12
CO ₂
TiO ₂	0.56	0.50	0.71	0.74	0.72	0.78
ZrO ₂	0.01	0.01	0.01	0.01	0.01
P ₂ O ₅	0.17	0.20	0.38	0.34	0.20	0.26
So ₃
Cl
F	(0.01)
S	0.01	0.01
Cr ₂ O ₃	tr	tr
V ₂ O ₅
MnO	0.09	0.08	0.09	0.08	0.08	0.10
NiO
BaO	0.04	0.07	0.03	0.07	0.04	0.02
SrO	(0.03)	(0.05)	(0.07)	(0.06)	(0.06)
Li ₂ O	(0.02)	(0.03)	(0.02)	(0.02)	(0.08)
Cu

TABLE III—Continued.

Lavas—Lassen Peak.

Ser. No.*	LP	CC	LP	LP	CC	LP
	25	1	35	20	3	45 (12)(13)
SiO ₂	57.27	56.62	55.55	55.81	54.71	63.21
Al ₂ O ₃	17.53	16.41	18.68	18.94	15.55	17.15
Fe ₂ O ₃	1.62	1.03	3.51	4.25	1.65	1.30
FeO	5.00	5.30	3.73	3.00	5.54	3.00
MgO	4.10	6.77	4.60	4.42	8.55	2.96
CaO	7.27	7.79	9.06	8.88	8.52	5.23
Na ₂ O	4.10	2.99	2.33	2.87	3.18	4.12
K ₂ O	1.17	1.49	1.05	0.78	1.23	2.10
H ₂ O+	0.28	0.31	0.35	0.35	0.26	0.31
H ₂ O—	0.14	0.03	0.01	0.09	0.03	0.04
CO ₂
TiO ₂	0.88	0.76	0.74	0.77	0.66	0.48
ZrO ₂	0.01	0.07	0.02	0.02
P ₂ O ₅	0.38	0.22	0.12	0.16	0.15	0.16
SO ₂
Cl	0.01	0.02
F	(0.01)	(0.02)
S	0.03	0.04	0.03
Cr ₂ O ₃	0.06	tr	0.06	tr
V ₂ O ₅	tr
MnO	0.12	0.10	0.10	0.09	0.07
NiO	0.07
BaO	0.03	0.04	0.05	0.02	0.03
SrO	(0.07)	(0.08)	(0.07)	(0.06)	(0.03)
Li ₂ O	(0.02)
Cu

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavas—Mt. Pelée.

Ser. No.*	MP	MP	MP	MP	MP
	4 (7)	5 (8)	6 (9)	1 (10)	7 (11)
SiO ₂	62.05	63.53	62.79	62.51	62.87
Al ₂ O ₃	17.99	17.02	17.61	17.56	17.35
Fe ₂ O ₃	2.11	2.80	3.36	1.94	1.54
FeO	4.13	3.25	2.66	4.15	4.31
MgO	2.21	2.08	1.98	2.12	2.08
CaO	6.48	5.83	6.15	6.19	6.05
Na ₂ O	3.39	3.59	3.27	3.22	3.41
K ₂ O	0.97	1.05	0.95	0.98	1.04
H ₂ O+	0.08	0.16	0.08	0.60	0.42
H ₂ O-	0.01	0.09	0.03	0.08	0.00
CO ₂
TiO ₂	0.50	0.47	0.50	0.50	0.46
ZrO ₂	0.003	0.02	0.01	0.02	0.01
P ₂ O ₅	0.23	0.16	0.30	0.20	0.23
SO ₃
Cl	0.03	0.02	0.02	0.09	0.09
F	p.n.d.	p.n.d.	p.n.d.	p.n.d.
S	0.003	0.003	0.01
Cr ₂ O ₃	0.00
V ₂ O ₅
MnO	0.14	0.14	0.14	0.14	0.16
NiO
BaO	0.02	0.00	0.02	0.02	0.01
SrO
Li ₂ O
Cu

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavas—Hawaii.

Ser. No.*	P 1919 (16) (17)	KMP 1923 (18)	KMA 1923 (19)	KAA (20)	K 1924 (21)	ML '26 1 (23)	ML '26 2
SiO ₂	50.19	49.33	49.42	50.50	47.45	51.82	51.34
Al ₂ O ₃	13.34	11.57	11.83	13.31	8.83	13.66	12.94
Fe ₂ O ₃	1.23	2.31	3.83	1.21	1.07	1.50	3.48
FeO	9.85	9.48	8.08	10.03	10.57	9.68	8.42
MgO	7.96	12.41	12.04	6.73	19.66	7.24	7.88
CaO	11.65	9.14	9.28	11.30	7.93	10.09	10.36
Na ₂ O	2.09	2.20	2.35	2.20	1.72	2.30	2.24
K ₂ O	0.54	0.44	0.59	0.53	0.13	0.30	0.37
H ₂ O+	0.09	0.11	0.16	0.26	0.07	0.11	0.04
H ₂ O—	0.00	0.01	0.02	0.00	0.01	0.01	0.05
CO ₂
TiO ₂	2.60	2.85	2.42	3.63	1.77	2.07	2.22
ZrO ₂
P ₂ O ₅	0.41	0.37	0.39	0.47	0.37	0.39	0.26
SO ₂
Cl	0.02	0.03	0.02	0.02	0.03	0.01	0.01
F
S	0.07	0.03	0.01	0.08	0.02	0.02	0.09
Cr ₂ O ₃	0.08	0.13	0.15	0.04	0.04
V ₂ O ₅
MnO	0.15	0.14	0.14	0.15	0.17	0.13	0.15
NiO
BaO	0.02	0.04	0.01	tr	tr
SrO
Li ₂ O
Cu

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Concluded.

Ser. No.*	Lavas—Hawaii		Lava— Niuafooua		Diabases	
	ML '26 3 A	ML '26	ML '26		Md 9 1	NJGD
	(24)	3 B	4	(25)	(30)	(31)
SiO ₂	51.55	51.67	51.38	50.37	51.28	52.40
Al ₂ O ₃	13.59	13.42	13.39	14.65	15.07	13.67
Fe ₂ O ₃	2.33	2.05	2.43	2.19	1.12	1.15
FeO	9.04	9.04	8.80	9.24	9.31	9.16
MgO	8.02	7.97	7.79	7.13	7.97	7.86
CaO	10.31	10.39	10.54	11.74	11.42	10.42
Na ₂ O	2.43	2.39	2.43	1.88	2.03	2.11
K ₂ O	0.27	0.27	0.28	0.31	0.27	0.64
H ₂ O+	0.07	0.26	0.09	0.13	0.39	0.69
H ₂ O—	0.02	0.01	0.03	0.03	0.09	0.23
CO ₂
TiO ₂	1.98	2.15	2.08	1.75	0.78	1.19
ZrO ₂	0.00
P ₂ O ₅	0.24	0.49	0.60	0.17	0.13	0.21
SO ₂
Cl	0.02	0.00	0.03
F	0.02
S	0.05	0.06
Cr ₂ O ₃	0.08	0.08	0.05	0.03
V ₂ O ₅	0.15	0.13	0.06
MnO	0.12	0.14	0.16	0.15
NiO
BaO	0.01	0.00	0.03
SrO	0.00
Li ₂ O
Cu

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

NOTES FOR TABLE III.

- (1) Dense black obsidian, Big Glass Mountain, California.
- (2) Pumiceous phase of same block.
- (3) Dense black obsidian (No. 4), Coso Mountains, California.
- (4) Coarsely vesiculated portion of same block as No. 3.
- (5) Dense black obsidian, Cerro Noagua, New Mexico.
- (6) Pitchstone, Cerro Noagua, New Mexico. Apparently a compressed pumice, or incipient pumice.
- (7) Hypersthene andesite, Mt. Pelée, Martinique, F. W. I. The series of 1902 lavas. A piece of the old summit pinnacle (Morne Lacroix) which rose above the rim of the old crater. Very fine-grained groundmass but nearly or quite holocrystalline with cavities containing tridymite.
- (8) Mt. Pelée. Portion of the "spine" of 1902-3. Groundmass contains pyroxene, feldspar, tridymite, and glass. Fragments of a highly feldspathic and more crystalline rock are present.
- (9) Mt. Pelée. Summit of new cone near eastern edge of spine of 1902-3. Ferromagnesian phenocrysts (probably hypersthene) are surrounded by reaction products of a deep red-brown color having strong birefringence and high refractive index.
- (10) Mt. Pelée. "Pumice from a nuée ardente July 1902. Lacroix." The cellular glass has few microlites. After heating in vacuo the phenocrysts in some parts of the glass were completely dissolved. Small amounts of hypersthene crystals were filled with a meshwork of glass and embedded in dark glass but no distinct reaction border appeared.
- (11) Mt. Pelée. Shell of a breadcrust bomb, 1902-3. Phenocrysts in a slightly bubbly light colored glass.

[In the Mt. Pelée series (Nos. (7) to (11), inclusive), SO_2 was determined instead of listing all sulphur as S_2 .]

- (12) Lassen Peak, California. A breadcrust bomb, 1915. Surface.
 - (13) Interior of same bomb as No. 12.
 - (14) "The volcanic activity and hot springs of Lassen Peak." Arthur L. Day and E. T. Allen, Carnegie Inst. Wash., Publ. No. 360, 1925.
 - (15) Kilauea lava dipped from the middle of the active lake in 1911 by F. A. Perret. See "Water and volcanic activity," Arthur L. Day and E. S. Shepherd, Smithsonian Report for 1913.
 - (16) Kilauea. Dipped by pot and chain by T. A. Jaggar. This and the following were parallel runs used to check the analytical method.
 - (17) Same as No. 15.
 - (18) Pahoe-hoe from Makaopuhi flow, 1923.
 - (19) Aa from Makaopuhi flow, 1923.
 - (20) Aa from an old flow within the crater.
 - (21) A peculiar lava erupted from an unknown depth in the 1924 explosions at Kilauea. It looks as though baked and slightly burned, but the ferric iron is not increased and may be slightly low. The olivines are iridescent and shot through with a brownish powder too fine to be determined.
 - (22) Kilauea. Lava brought up on the sounding-rod used by Jaggar. Lava not analyzed.
 - (23) Pumice phase of the 1926 eruption of Mauna Loa. From the summit crater, collected by T. A. Jaggar.
 - (24) From the 1926 eruption of Mauna Loa (Jaggar) from the 1400-foot level. No change could be found.
- [Determinations of F_2 , SrO , and Li_2O were made much later; the analytical sum has not been readjusted thereto.]
- (25) Lava collected by T. A. Jaggar, Niuafoou Island, 1930. From 1929 eruption.
 - (26) Granite from Stone Mountain, Georgia. Our standard granite used in a number of different studies.
 - (27) Granite from North Jay, Vermont.
 - (28) Granite from Barre, Vermont. Contains calcite.
 - (29) Marvine laccolite, Henry Mountains, Utah. Selected as showing the least alteration of the specimens collected. The feldspars of most specimens were cloudy.
 - (30) Diabase from near New Market, Maryland. Our standard diabase for various studies.
 - (31) Diabase from Granton, New Jersey. Shows slight alteration on careful examination.

LASSEN PEAK ANALYSES.

- LP/32 Schistose rock from just below the present peak.
- LP/18 South wall of the old crater slope. Lookout Point.
- LP/2 Top of cliff just above Drakesbad.
- LP/34 Gray dacite one-third way up peak.
- LP/7 Loose inclusion in flow near west side of crater.
- BH/1 North wall above Bumpass Hell.
- LP/10 Lava (old?) flow in crater. West end near edge of mass.
- LP/28 From shore of Lake Hellen.
- BH/3 Southwest lip of basin, Bumpass Hell.
- CC/6 Flow between Snag and Grassy Lakes.
- LP/21 Inclusion near source of "flow" of 1915 in Lassen Peak crater.
- CC/7b Trail between Snag and Grassy Lakes. Half a mile from Grassy Lake.
- LP/25 Basalt flow between Tartarus and Geyser.
- CC/1 Wall rock, source of the Cinder Cone flow.
- LP/35 Inclusion in gray dacite one-third way up southeast slope of Lassen Peak.
- LP/20 Inclusion in old wall of the Lassen crater. Large block with dates carved in it going back to 1884.
- CC/3 End of Cinder Cone flow containing a few very large quartz masses.
- LP/45 Lassen Peak crater. From the 1915 extrusion described by Day and Allen, op. cit., p. 46.

looked a small amount of sericite present.¹⁹ As to the effect of alteration on the volatile content, a little arithmetic may be illuminating. Take the figure 30 cc./g. of rock and note that this means about 90 cc. per cc. of rock of density about 3. A cubic meter of such rock would yield about 90 cubic meters of gas at 1200°, and a cubic kilometer might yield an amount of the order of 90 billion cubic meters of gas if all gas were available. Our table shows that with relatively slight alteration this figure will be trebled, and with noticeably altered material, increased indefinitely.

Table III is added to give the chemical analyses of all materials studied in Tables I and II, and has been extended to include all the analyses which we have made on the suites of rocks from which we selected those examined for volatiles. The remaining analyses may be of service to petrologists, though many of them, especially the Lassen suite, were made before we decided that no advantage would result from out-gassing all the series.

Before taking up the geological implications of these gas studies we shall summarize the results thus far.

The following inferences seem to be justified:

1. The distribution of the volatiles in rocks and lavas is largely fortuitous.
2. There is as yet no reasonable way in which either the composition or quantity of the primitive magmatic exhalations can be deduced.
3. This uncertainty follows from the ineluctable contamination to which such gases are subjected on their way to the surface of the earth.
4. With the Kilauea crater as an example it has been shown how this contamination occurs and why no constancy of composition is to be expected.
5. Approximate figures are found for the minimum volatile content of unaltered rocks and lavas, and some light is thereby thrown on the questions of condensation, redistillation and recondensation with the concurrent unpredictable enrichment in one or another element. The importance of this process is emphasized.
6. Chemically the volatiles show the predominance of water, 80 per cent or more, the nearly complete oxidation of the gases, and the absence of notable amounts of hydrocarbons and rare gases.

¹⁹ Obviously there is nothing to be gained by increasing the number of analyses of the altered rocks. There may well be some profit in a series of such analyses if done in connection with an elaborate chemical and geological study of some particular rock mass.

It seems clear that chemical reactions do not constitute the important factor in volcanism that some had supposed. On the other hand, this investigation opens up a more promising field which concerns itself with phenomena much nearer the earth's surface and more accessible to investigation. To this aspect we may now turn our attention.

Once we know definitely what volatiles are present in igneous rocks and their average minimal amounts we may turn to the special considerations and investigations which grow out of our observations. Always in the background hovers the question as to the condition in which the volatiles are present.

If we begin with the simplest case, gases dissolved in solid glassy obsidian, the answer is apparently simple. The gases are in solution in the glass and our interest centers on the possible solubility of these volatiles in the glass. Here we are on solid ground, for we have glasses with determinable quantities of volatiles in them and we have also Goranson's work on the solubility of water in these particular silicate solutions. The field specimen can be checked against the laboratory determinations.

In the first section of Table II we have "selected" field material. We collected a great many obsidians from many sources. This material was then exhausted in vacuo and the water content determined. With a few notable exceptions the majority of obsidians tested were astonishingly dry, for example, No. 1 and No. 3 (Tables II and III) may be taken as typical. The water content is of the order of 0.01 per cent taken on the unground material and the total volatile content is only about 1.5 cc./g.

Of the dozens of obsidians tested, this dryness is the outstanding, if irritating, characteristic. Adjacent vesiculated parts of the same block, such as No. 2 and No. 4 (Table II) show more gas, but one can not tell with certainty how much was in solution in the glass and how much adsorbed on the surface.

Numbers 5 and 6 are of quite different behavior. These two specimens we owe to Doctors Ross and Larsen, who collected them near Cerro Noagua, New Mexico. No. 5 is a splendid black (transparent in thin section) glass with over one per cent of volatiles, and yields 55 cc./g. It is the best material thus far received, though it was not found in place and a further supply has not been obtainable on search. No. 6 is a cream-colored rock with somewhat resinous fracture like a

pitchstone and contains a few large albite phenocrysts which appear to be undissolved residues rather than the beginnings of crystallization. It was examined by H. E. Merwin, who found in it very fine elongated vesicles.²⁰ Computed to a dry basis, these two rocks are identical (see Table III). Although the water may be in solution in both glasses, the physical behavior is different. Upon being heated, No. 5 remains unaltered until (depending on the time and temperature) at 800° after 15 minutes vesiculation begins and continues until the gases are expelled. The mass puffs up into a pumice with large thin-walled vesicles. No. 6 remains unaffected under these conditions and can be induced to puff only by very rapid heating to nine hundred or a thousand degrees. The difference is that No. 5 loses only surface water until vesiculation begins—that is, the water is held firmly in the solid glass. No. 6 begins to lose water as soon as heat is applied and evidently there is no difficulty in the escape of the volatiles. The very slight puffing of this glass seems to be confined to water in solution in the septa between the pores. Heated in vacuo to 1200° for some hours, the chips of No. 6 slump down to a viscous clear glass, whereas No. 5 puffs and after losing its water is too viscous to flow together under its own weight, though, given time, it slowly slumps down.

In heating these obsidians one very important phenomenon appears at once. For these "wet" glasses (and the same would be true of the mother liquor of a crystallizing magma) a rapid change in the apparent viscosity is caused by relatively insignificant concentrations of volatiles, when a block of No. 5 (1.25 per cent volatiles) reaches the vesiculating temperature it flows, i.e. froths, around and through small obstacles, or in a tube it froths all over the inside. But once the volatiles are out, the septa and shreds of glass remain indefinitely rigid. It requires much time and a much higher temperature before the mass begins to gather itself together again. This quick shift from

²⁰ There is no satisfying criterion by means of which one can discriminate between an incipient pumice, that is, a magma whose pressure has been reduced enough to permit vesiculation to start and which if brought to the surface would expand to a pumice, and a magma supersaturated at the pressure and temperature acting on it, so that the second phase, silicate in water, appears in accordance with Goranson's data. We have one tuff (showing 5.3 per cent total H₂O) from the Salton Sink region many of the glass shards of which were found by H. E. Merwin to contain liquid with various-sized bubbles. Such material seems to fit the two-phase picture. The absence of such vesicles in the Cerro Noagua No. 6 would seem to place it in the incipient pumice class. No sharp dividing line would be expected.

fluid to rigid glass has obvious importance both for volcanology and petrology.

Heated in vacuo, both No. 5 and No. 6 lose water; surface water escapes rapidly, and the remainder diffuses out slowly. Thus an 8 gram cylinder of No. 5 lost only 0.006 per cent in weight (about 7 per cent of its total water) in three months at 400° C. Under similar treatment, No. 6 lost 2.3 per cent (70 per cent of the total) out of its total of 3.25 per cent water in 1 hour and at only 300°, after which, rapid loss in weight the rate dropped to about 0.01 per cent in twelve hours. Since the surface of No. 6 is indefinitely greater than that of No. 5, only the general form of the curves is comparable. To obviate as far as possible the effect of the difference in surface, both No. 5 and No. 6 were powdered, placed in a capsule, and heated at 300° in vacuo. In thirty minutes No. 5 lost 0.16 per cent (about ten per cent of its total water) and No. 6 lost over 70 per cent of its content. After nine hours No. 5 had lost less than 30 per cent, and No. 6 about 87 per cent. The experiment can not be conclusive, but it points to the same inference as that made from the observations of the coarser material.

The search for a series of obsidians with increasing water content has been a bit trying, for the water is not uniformly distributed throughout any given field exposure. Only by testing each specimen in the field can one avoid collecting an unconscionable load of dry material.²¹ Messrs. Greig and Schairer made some collections in the New Mexico area, testing the material with a blowpipe. From one exposure they secured a number of good specimens, but none with a high water-content. It was possible, however, to select from their collection a series running between one-tenth and eight-tenths per cent water. This series is very useful for experimental purposes as we are not yet able to make synthetic mixtures in sufficiently large pieces for all the tests one may wish to apply. Certain important tests can be made with the present series. The significant fact is that most of the dense glass found in the field contains very little water and can flow if at all only at temperatures far above those which for other reasons we have associated with eruptions. We have made a number of experiments touching the diffusion rate of water in obsidians.

²¹ This is the more surprising because great masses of obsidian are known where there is no difference of chemical composition over great areas (Little and Big Glass Mountains, Table III), and although these masses are usually uniformly dry, occasional specimens may occur with varying degrees of wetness. Similar conditions obtain at Cerro Noagua.

The data are not yet ready for discussion, but we may say that up to 1.25 per cent of volatiles the rate is not noticeably different from that expected according to the usual diffusion formula. The implication is that water does not enter or leave these glasses with any unusual ease at temperatures up to 500° at any rate. Dehydration studies at temperatures above 500° are not feasible because above that a glass with one per cent or so of water will slowly develop vesicles, and at lower temperatures the rate of weight loss drops to practically zero. As Goranson's studies show, we are not to expect a high water-content in any glass which arrives at the surface hot. Fifty atmospheres of pressure, or more, are required to prevent these glasses from vesiculating. It follows that we may only hope to obtain water-rich material from dikes or sills which have been exposed by erosion, because notably wet glass will vesiculate or explode if brought to the surface at any temperature at which it is able to flow.

Although the time factor enters into our experiments and confuses our observation and deductions in both field and laboratory, we can show experimentally that the viscosity of these and presumably all magmas is profoundly altered by the amount of water present. For example, a weighted prism of the dry Coso Mountain glass (Table II, No. 3) showed no bending when heated 24 hours at 575° C., and the wet Cerro Noagua glass (No. 5) was slightly bent and breadcrusted under the same conditions. We know that in 15 minutes at 900° the Coso glass remains unaltered and the Cerro Noagua has expanded into a very light pumice. But for anything one would call flow in the field sense, temperatures above 600° are needed even with the Cerro Noagua glass. However, this same glass, given time, will start vesiculating at 600° or even lower, and with rising temperature vesiculates more and more readily unless the pressure is high enough to hold the water in solution. The time factor, that is, the time required for vesiculation to get under way, enters the problem unpredictably except for the general rule that the more water present the more readily vesiculation starts. This point is nicely shown in the following experiment, which is similar to the Seger cone method of temperature determination. Place a series of small chips of obsidian of differing water content on a refractory plate and set the plate in the furnace for a fixed time and at a series of temperatures. Take, for example, obsidian chips containing respectively 0.1, 0.3, 0.5, 0.7, and 1.2 per cent total volatiles

(we use gases, volatiles, and water interchangeably because water is so overwhelmingly dominant), and start at 800° with a 15-minute heating period. Except for the last (1.2 per cent water) which is unstable above 600°, none will show any change. The one with 1.2 per cent water may vesiculate. With a longer exposure or with slightly higher temperature, the 0.7 per cent glass may show changes. At 900° the 1.2 per cent will at once expand to pumice and the 0.7 per cent may start to vesiculate; the others remain unaffected except that at above 700° all these obsidians bleach more or less and do not darken on cooling down. As the experiment is continued the less hydrated samples will vesiculate in regular order as the temperature is raised, until at about 1200° the material with lowest water content will in time show a few scattered vesicles. The degree of vesiculation, the size of vesicles formed and the thickness of the septa between them, vary also with the water content. For the samples with little water content, temperatures around 1200° or more, as well as ample time, will be needed before they will deform under their own weight. In fact, the dry glass is so astonishingly rigid that we are not yet able to imagine its flowing in the ordinary sense of lava flows. That it may be slightly plastic is evident in the field but it seems more likely that these dry masses reach the surface carried along with and surrounded by a shell or shells of more fluid material, and that the latter is for the most part carried away explosively.

The above-cited experiments on the relation of volatile content to viscosity have an important bearing on the mechanism of extrusion and lava flows. In the interval where vesiculation occurs the glass is notably fluid, the expanding pumice can froth around and between obstacles. But once fully expanded, that is to say, once the volatiles have been liberated, the foam becomes rigid. Unlike most foams known to us, this material is no longer mobile. Expanding into a crack or fissure it can effectively seal it. Masses of foam act like solid objects in the magma. Instead of increasing mobility as with ordinary froths, this rock foam decreases it and may block movement by clogging the pathway. The reverse reaction is of course possible. A mass of this foam if trapped and subjected to heat and water at sufficient pressure will of course collapse and become fluid again. These observations are helpful when we try to picture the mechanism of flowing lava, of extrusion, or eruption. The fact that the effective viscosity varies so greatly

with relatively small change in the volatile content is very illuminating!

The experiments outlined above show that the time interval varies with temperature, pressure, and volatile content. Vesiculation both chills and stiffens the mass and some time must elapse before the temperature is readjusted to a point where further vesiculation or explosion will occur. This mechanism should be particularly noticeable for the final mother liquor of a partly crystallized rock.

Since the rate of diffusion of water vapor through the obsidian shows no unusual speed, that is, seems to obey the usual formula, and does not behave in a special manner, like hydrogen and palladium, it follows that these huge masses of dry obsidian as found in the field can hardly be thought to have lost their water content after arriving at their present emplacement. Apparently they have never been very wet. The possibility exists that these dry masses may represent lenses carried along by the wetter, less viscous envelopes. The Mono Craters as described by Russell²² seem to have been formed in some such fashion. Each crater has a central plug of dry and rigid glass. In a few places the plug shows a slight bending, or overhang, of an otherwise vertical outer surface. Most of the plugs were evidently not plastic enough to bend under their own weight. The edifice is in all cases constructed of pumiceous material and ash. There is no way of knowing whether the entire glassy mass was originally laid down as a dry core with wet envelopes or whether the envelopes represent a reactivation of an originally dry magma, where the reactivation had not yet penetrated to the core before eruption occurred.

With the less acid crystalline rocks, andesites and dacites (Table II) we find 6 cc./g. to be the common and presumably average residual gas content of our selected material. The exception, MP 1 (Tables II and III) being a chilled breadcrust surface. The Lassen Peak material contains more gas and also shows slight alteration. This figure, 6 cc./g., continues through the Hawaiian lavas, with one notable exception, No. 21.²⁸

²² Russell, I. C.: *Volcanoes of North America*, p. 217, 1910.

²⁸ This No. 21 is a peculiar olivine basalt erupted during the phreatic explosions of Kilauea in 1924. It reached the surface apparently barely red hot, and in blocks, but not as fresh lava. As the analysis shows, it is not a fumed and decomposed rock. The iron is normal, it is not oxidized, magnesia is naturally high, and the alkalis a little low. The rock appears normal enough except that the olivines are iridescent. The indications are

The plutonics examined show a different order of "normal gas content." Here (Table II) the figure is about 30 cc./g., but it will be much greater if alteration of any kind has occurred during the rock's history.²⁴ Unfortunately, there is no clue as to what part of the volatiles belongs to the rock initially and what part is secondary. We can not determine the pore space or surfaces and can not distinguish between surface chemical reactions and adsorption. There is a tendency toward a low CO₂ for unaltered rocks, and where sulphides are present H₂S will appear in the gases given off. The sublimates as deposited in the SiO₂ tubes on out-gassing these rocks show much SiO₂ along with varying amounts of Fe, Cu, Zn, Mo, etc.²⁵ The study of such sublimates and their relation to fumarolic and mineral deposits has not yet been undertaken.

We do not know in what condition the gas is held in the rock and we do know, as Chamberlin found before us, that it is not a simple adsorption. The gas pumped out is not reabsorbed in any notable degree, just as the water pumped out of obsidians at relatively low temperatures, 300-500°, is not restored on subjecting the rock to an excess of water at atmospheric pressure. Then, too, as Chamberlin found, even though

that we have here a rock which has been reheated, but in an effectively neutral atmosphere. From the total volatiles alone (compare the other Kilauea lavas cc./g. in Table II) we get our idea as to the treatment to which this lava has been subjected just as an excessive gas content indicates a different record.

The absence of oxidation is suggestive of conditions at no very great depth in this volcano. The extremely porous nature of the Kilauea edifice would lead one to expect a free circulation of air and oxidizing conditions, yet these 1924 explosions which eviscerated the core of the volcano brought this and other products of a non-oxidized character to the surface. For example, there had existed for many years a series of hot cracks (the Devil's Kitchen) which exhaled a mixture of steam, SO₂, SO₃, and free sulphur. The surface rock was disintegrated to sulphates and sulphur, giving the impression of intense oxidizing action, and yet from beneath this area large quantities of ferrous magnesium sulphate were erupted. Oxidation, then, seems to be a surface phenomenon which requires a much greater freedom of air circulation than even the Hawaiian volcano structure permits. This point is significant for those who seek to derive volcanic heat from oxidation and reduction reactions. The Hawaiian type of edifice is so very open to air circulation that if such reactions are important they should be noticeable here. They are not.

²⁴ We found that the figure of about 30 cc./g. could be readily explained by taking into account the volatiles in micas and hornblende, and some adsorbed water, that is, the average minimum content as computed from the hydrous minerals is of the same order as the value found experimentally for carefully selected granites. If there is more than this amount of water and it is unable to escape readily, then alteration will be noticeable.

²⁵ A preliminary spectroscopic examination for which the writer is indebted to his colleague Dr. E. G. Zies.

the gas be partly reabsorbed, it will have undergone a change of composition when re-evacuated. Not being able to determine the surfaces and dimensions of the cavities present we have no way of linking our analyses to what is now known about adsorption phenomena. We have found that traces of alteration (of whatever origin) increase the total volatiles notably above our averages for the best material obtainable and this increase in volatile content runs parallel with increased alteration.

For the granites Goranson²⁸ has given us our first definite data as to their melting temperatures. It has long been believed that instead of being a high-temperature rock as the early studies of the melting temperatures of rocks implied, granite was formed at relatively low temperatures, 500-600° C. being a not wholly absurd figure as judged by the minerals present. Goranson found that at $700 \pm 50^\circ$ the Stone Mountain granite No. 25 would be completely liquid with 6.5 per cent water at a pressure of 1000 bars. But our tabulated data involve no such water content; evidently the volatiles have largely escaped or were not present initially.

A relatively low water concentration would give to the last portion of the crystallizing mother liquor a rather high and at times explosive (Mt. Pelée) volatile content, yet if we consider the relatively few plutonics which show cavities or pronounced alteration by their own volatiles the implication is that their volatile content is not particularly high. Of course this point is a matter of opinion and not subject to proof. However, if one runs over in one's memory the innumerable igneous contacts where apparently little or no alteration showed, and other areas not apparently different as to the facilities for escape of volatiles in which profound alteration appears at the contact, it seems to us a fair inference that while in general the volatile content of the magma has not been at all high, in special cases there has evidently been a concentration of volatiles either in the magma or in the enviroing rock which has produced great changes. Those who prefer to consider the volatile content of magmas as high because of the enormous quantities of gas given off by volcanoes should not overlook this possibility of local enrichment either of the magma or country rock. That a magma can absorb water was shown in Adams and Goranson's work. Since they find that the solution of water in the

²⁸ Goranson, R. W.: The solubility of water in granitic magmas, *Am. J. Sci.*, 22, 481, 1931; Some notes on the melting of granite, *ibid.*, 23, 227, 1932.

melt is an exothermic reaction, the much disputed question of whether a magma can take up water, meteoric or other, and thereby be rendered "explosive" is answered in the affirmative.²⁷

Of course our data can not tell us how much gas may have been in the lava before it reached the surface but we have Goranson's work which shows that not more than ten per cent of water can occur in a granitic magma without the appearance of a second phase, silicate dissolved in water. That being true, the relative scarcity of drusy granites indicates that we seldom have to deal with such excessive volumes of water in granites. Goranson shows that at 900° nine per cent of water will form a second phase, that is, develop drusy cavities at 3000 bars pressure corresponding to about eleven kilometers depth while with only six per cent of water cavities should appear at a mere four kilometers. It is a reasonable inference that such excessive amounts of water are uncommon. On the other hand, drusy plutonics are known, showing that under some special conditions these high volatile concentrations do occur.

We must not overlook the important fact that certain special conditions are required before a magma can absorb water. Some volcanologists have written as though all that was required was for a magma to come in contact with meteoric water. This is no more true in depth than at the surface, for while steam explosions do occur when a hot rock comes in contact with water, we now know that for the water to be

²⁷ A cubic kilometer is no great volume of the Earth's crust; much larger lava outpourings are common. With only the average volatile content for unaltered rocks (30 cc./g., a few tenths of a per cent by weight) a cubic kilometer might yield some ninety billion cubic meters of gas if raised to 1200°. To pass this volume of gas through a 100-meter conduit (i.e. an orifice of 7854 square meters) in twenty-four hours requires that the gas issue at a rate of 477,000 meters per hour, 296 miles per hour or nearly five miles per minute. With a more restricted orifice the phenomena would be even more impressive.

One would not expect any such complete release of volatiles, but the figures serve to indicate that a few hundred degrees rise in the geotherms of a region, especially if the rocks have been previously enriched in volatiles to the extent of only a per cent or so, will release enormous volumes of gas. Enough gas can evidently be obtained from the country rock to account for many volcanic phenomena without postulating excessive concentration of volatiles in the advancing magma.

If the water content is of the order of 3 per cent as with the pitchstone No. 6, or of 5 per cent as with some others, then the available gas reaches an amazing volume. These very "wet" rocks are comparable to explosives and act similarly if suddenly erupted. For example, black powder yields only 1500 cc./g. at 1200°, 760 mm., and the "high" explosives about 4300 cc./g. In comparison, the material with which we have been working does not class as a high explosive though Mt. Pelée developed such qualities at times.

absorbed by the magma this foreign water must be at such a temperature and pressure that the reaction moves in that direction, otherwise the heat merely evaporates or distills the water. Yet water under sufficient head or water trapped by impervious strata will be absorbed by advancing magma once the conditions are fulfilled.

It seems to us that a more reasonable and illuminating picture of subterranean phenomena is obtained if we take into consideration what may be expected to happen when magma from below advances into the crustal layers. The most casual field observation teaches us that although some large areas have been little disturbed, many show not one but repeated invasions of magma. For example, in the Crazy Mountains, or the Highwood Mountains of Montana and the neighboring country, as at Shonkin Sag Laccolith, we have a much troubled area shot through with sills and dikes in a most puzzling manner. For the majority of contacts observed there was no apparent alteration of the country rock but at certain places apparently the volatiles were trapped in such manner that intense alteration was produced (Haystack Butte). With the mechanism of injection we need not concern ourselves; it is sufficient that it occurred.

On a simpler scale, let us picture what happens to the volatiles of the country rock when subjected to such treatment. We shall assume (which is of course not true) a uniform distribution of volatiles in the country rock. If this area is invaded by hot magma, this by raising the geotherms will cause the volatiles in the affected area to move over to be recondensed in cooler areas. In addition, volatiles brought up by the magma may be expected to penetrate the area and be condensed also. Some of the strata of areas penetrated by the magma may be relatively impervious to the volatiles or their condensates. We have then a spotty distribution of volatiles scattered through the country rock. This is the fundamental explanation for what we have already observed in our analyses; that while rocks selected for the absence of alteration show a common volatile content, altered rocks may show many times that quantity; that the quantity which we find in any rock will be purely a chance figure depending on the past history of the rock.

Now it is common observation that the first phase of an eruption sends, primarily, the halogens (the most volatile) outward or upward, and it is equally true that the dying out of the eruption is accompanied by the exhalation of the sulphur

gas and other less volatile constituents. We are to expect, therefore, an enrichment in halogens at the greatest distance from the heated areas and enrichment in sulphur nearer the dike or conduits. A new rise in temperatures, as at the beginning of an eruption, will move the halogens first, the rest following according to their volatility. It is obvious that if the country rock is inhomogeneous (as it usually is) then some areas will be relatively impervious and others will allow free passage to the moving vapors. Again we have an unpredictable distribution of volatiles.

If, now, after a period of rest the area is again injected with magma, not only will new volatiles be introduced but old ones will again be set in motion. Certain areas have now been several times fumed and cooled. It is easily fancied that conditions being right this mass may have its temperature raised and its volatile content so increased that it will be either remelted or partially melted and rendered potentially mobile. It does not strain the imagination to account in some such way for the appearance of a rhyolite or andesite from a crater initially basaltic or vice versa.

Something of this sort may have happened at Katmai and the Valley of Ten Thousand Smokes. Here we may suppose that we have a sill of new magma injected beneath an old water-soaked valley. Had the load above been sufficient it was entirely possible that even if the magma was not already saturated, the water from the country rock would be absorbed until some balance was attained or until a break or other dynamic disturbance set it free. If some of the magma was initially more hydrated or acquired more water than other portions, or if the surface of the sill became hydrated, then there would be a very reactive shell around a mass which might be hot but less mobile in the interior. In such a case the Novarupta plug, which in some respects seems similar to the Mono Crater plugs, would be one manifestation while the lava which gave the "sand flow" also fits into the picture.

Meanwhile we must suppose that the long accumulation of volcano residues in the old valley has been providing its own kinds of entertainment. For our present purposes it is not too important whether the above picture of Katmai is the real picture or not, but it may serve to indicate why the gases in rocks are unpredictable in both amount and distribution and yet may be very important in relation to volcanology and related problems. The more one looks at the problems with this pic-

ture in mind the more clearly many field observations seem to fit into it. Hybrid rocks, and the slow digestion of xenoliths become intelligible since we are in this case dealing, not with the initial energy of the cooling magma but with energy from other sources working on separated portions of the old magma. That means that equilibrium conditions will be quite different. It means also that in a much disturbed region rocks may be worked and reworked not once but many times and elements not usually considered mobile be variously transported, concentrated, and recombined.

With Goranson's study of the melting of granite and the relation of water to it, we can see that the partial or complete remelting of the acid rocks, at any rate, can occur and at no great depth. The temperature observed at volcanoes average somewhere between 1000 and 1100°. To melt a granite, assuming a supply of heat from an invading magma and sufficient water under pressure,²⁸ involves not more than 750° and for partial remelting perhaps 600°. The solution of water in a magma is accompanied by a heat evolution as yet undetermined, but known to be large. But whether these speculations as to volcano mechanisms be true, partly true, or sheer nonsense, we still have left the irregularity of total volatiles, and from Goranson's studies ample means to explain the altered condition of most plutonics. The zoned and fractured feldspars may involve more movements than we formerly thought possible, but we must allow not only the reactions involving water, but also the secondary ones involving CO₂,²⁹ the halogens, and sulphur. We no longer need, as formerly, to try to explain such changes exclusively by shifting pressure during crystallization of the primary magma. It is evident that an attack can now be made in this formerly impregnable field of study. To this work our apparently negative results contribute their mite for purposes of orientation.

²⁸ Goranson's data also imply that meteoric water given opportunity need penetrate to no astonishing depth before the hydrostatic pressure becomes sufficient to enter into the reaction if the temperature has been raised to five or six hundred degrees by any mechanism one wishes to assume. The observed fact that some deep mines and bore holes are very dry is cancelled by the fact that others are very wet. Mines in highly porous strata can not be extended to great depths.

²⁹ Feldspars are evidently surprisingly reactive (see C. N. Fenner: Bore-hole investigations in Yellowstone Park, *J. Geol.*, 44, 225, 1936). We may expect further any of the alkali-rich minerals to break down at least superficially in a water-CO₂ mixture to form various hydrated-carbonated mixtures whose effect on the gases potentially available will be unpredictable.

Some of these considerations may seem elementary, but they are not necessarily so to the chemist or laboratory worker who has some difficulty in extrapolating from test tubes to batholiths. To these we would point out, as we too have had to learn, that the earth's crust may be "solid" but is only relatively so, and it is certainly not static or dead. When we take into account the volatiles in the minute pores of the rocks, and the shift of these with the continuous changes in temperature and pressure, the effects of loading and unloading due to erosion, isostatic readjustments, shifting geotherms, and the continuous bending up and down due to the earth tides, the picture is that of moving, breathing masses, in constant flux.

ACKNOWLEDGMENT.

Throughout the years during which this work has been in progress the writer has been obligated to all his colleagues for both service and advice. In particular he is indebted to Arthur L. Day, who initiated this line of investigation, and to H. E. Merwin for never-ending assistance. To L. H. Adams, R. W. Goranson, and E. G. Zies for unfailing support is he deeply indebted. To these may he express his appreciation. However, none of these is in any way responsible for whatever may be felt to be fantastic in his inferences.

in a coal mine, the Gates Mine of the H. C. Frick Coke Company, a subsidiary of the United States Steel Corporation. I was interested to learn recently from W. O. Hickok, who was doing geologic mapping in Fayette County at the time, that he had found fragments of the Pittsburgh coal included within the peridotite. Mr. Hickok was kind enough to send me one of these specimens (No. 467B) on which a part of the experiments described below were made. I subsequently visited the mine and secured specimens of the dike rock, the bordering coke, and the unaltered coal.

Mr. Hickok's specimen was about 8 x 12 cm. in section, somewhat rounded. It lay within 6 inches (15 cm.) of the western wall of the dike, at a place where the dike was 4 to 5 feet in width. The bordering peridotite showed some effects of cooling in a slight refinement of the grain size.

EXPERIMENTS ON INCLUDED COAL.

A program of laboratory tests on some commercial electric furnace controllers offered an incidental opportunity to try the effect of long-continued high temperatures upon the Fayette County coal inclusions. Small angular fragments of the coal inclusion, 1 to 2 mm. in diameter, were sealed in evacuated Pyrex glass tubes of 4 mm. inside diameter. Some of the specimen tubes were 6 cm. long; such a tube, when placed inside an Alundum boat at the middle point of the platinum-wound electric resistance furnace, 29 mm. inside diameter, were uniform in temperature within about 10 or 15° C. Other specimen tubes were 22 cm. long; such a tube, when the end containing the coal specimen was placed at the middle of the furnace, projected a few centimeters into the outside atmosphere.

The results of these experiments, which turned out unexpectedly definite, are shown in Table I. No change whatever could be observed in the fragments until a certain fairly well defined temperature was attained, whereupon the tube became coated inside with a deeply colored distillate of tar.

The experiment is not complete without a parallel test of the unaltered coal. No specimen being available, I had to wait about a year until there was opportunity to visit the locality and secure a specimen from the Gates Mine. Specimens of the Pittsburgh coal were secured about 100 feet from the dike, at

TABLE I.

Effect of Laboratory Heating on Coal that Has Been Included in and Altered by Peridotite.

Specimen No. 467 B.

Sub-Specimen	Temperature, °C.	Time, hours	Tube Length, cm.	Effects
a	68-84	17	6	Appearance unchanged.
a	111-120	20		Appearance unchanged.
a	187-206	22		Appearance unchanged.
a	299-320	87		Appearance unchanged.
a	463-480	20		Appearance unchanged.
a	612-617	21		Tube coated inside uniformly with brown transparent coating.
d	511	½	22	Drops of colorless liquid (water?) condense in colder end of tube.
d	504-519	½		Drops colored light brown.
d	502-510	141		Light brown coating in first 2 cm. of tube.
d	556-563	45		Deep brown transparent coating over inside of hot part of tube.
d	563-575	168		Coating deeper color, fragments not fused.
b	643-654	140	6	Tube exploded, coal destroyed.

a cross section where the dike was about three to five feet wide and where its contact effects could not be observed for a distance of more than one foot into the coal. Tests of this unchanged coal were made in a sealed evacuated Pyrex tube in the controlled furnace, with the results shown in Table II. It is evident that the coal begins to distil at least 200° below the

TABLE II.

Effects of Laboratory Heating on Unmetamorphosed Coal.
Specimen No. 517d. Tube 22 cm. long.

Temperature, °C.	Time, hours	Effects
149	17	Unchanged.
192-205	71	Barely visible brown color in tube.
247-249	70	Some surfaces a little cracked and roughened.
268-271	19	Cloud of small colorless drops at cold end.
269-274	70	Ring of drops of light brown tar at cold end.
354-359	8	Orange-yellow tar distillate forms.

temperature at which the natural coke first gave a tarry distillate.

The results set forth in Tables I and II indicate that the coal included in the dike has been previously heated to at least

480° C., but has never been heated to 550° C. From these results its probable upper temperature may be placed at $520^{\circ} \pm 30^{\circ}$ C.

ANALYSIS OF INCLUDED COAL.

In looking about for some other method of estimating the temperature to which the included coal had been heated, I learned of H. H. Lowry's experiments on the effect of temperature on residual hydrogen in coals, charcoals, and similar products formed by the thermal decomposition of compounds of carbon, hydrogen and oxygen. Lowry's published data⁴ show remarkably consistent correlation between the percentage of hydrogen (on an ash-free basis) and the temperature.

Subsequent investigations, not yet published, and also an analysis of the large amount of data available in the publications of the United States Bureau of Mines, confirm the correlation of residual hydrogen with temperature and extend it to residual oxygen and nitrogen. It would appear that a carbohydrate breaks down into a structure of carbon atoms which has a fairly definite set of available spaces for hydrogen, oxygen, and nitrogen atoms, and these available openings decrease in number in a definite way with increasing temperature.

Doctor Lowry was kind enough to offer to have an analysis made of the inclusion from Fayette County, in the Coal Research Laboratory of the Carnegie Institute of Technology in Pittsburgh, of which he is the Director. The analysis was made by Mr. Frank C. Silbert, with the results shown in Table III. The percentages are calculated to a dry basis, the sample having 0.36 per cent moisture as received.

TABLE III.

Composition of Coal Inclusion from Peridotite.

Fayette County, Pa.

Carbon	72.12
Hydrogen	3.98
Nitrogen	1.69
Sulfur	0.82
Ash	17.32
Oxygen, by difference	4.07
	<hr/> 100.00

⁴Lowry, H. H.: The significance of the hydrogen content of charcoals, J. Phys. Chem., 33, 1332-1342, 1929.

Doctor Lowry's estimate of the maximum coking temperature from the analysis given in Table III is as follows:

From hydrogen	450° ± 10°
From oxygen	440° ± 20°
From nitrogen	410° ± 70°

He remarks in a letter: "I may confess that I was somewhat surprised at the excellent agreement of estimating temperatures from these three elements." The agreement with the value 520° C., that had previously been reached from my crude distillation tests described in Table I, is even more surprising.

DISCUSSION.

The geochemical puzzle posed by these results is this: Peridotite is an orthosilicate rock, consisting mainly of the orthosilicates of magnesia, lime, and ferrous iron, $2\text{MgO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $2\text{FeO} \cdot \text{SiO}_2$ (forsterite, di-calcium silicate, and fayalite, respectively). No such orthosilicate mixture has been observed in the laboratory to melt lower than 1093° C.⁵ Yet here is evidence that a peridotite magma has penetrated long distances into sedimentary rocks while it was at a temperature in the neighborhood of 500°.

Many specimens of these peridotites from western Pennsylvania, western New York, and Kentucky show a considerable proportion of carbonate. This is true of the specimens that I collected in the Gate's Mine. This carbonate has often been assumed to be a result of weathering but Honess and Graeber⁶ have shown, by examination of a similar occurrence, that some of the carbonate may be primary, while the greater part of it may be interpreted as the result of hydrothermal alteration immediately following the intrusion. Dikes even higher in carbonate than these are regarded by Daly⁷ as true magmatic intrusions.

Hess⁸ has summarized the characteristic relations of the serpentinized low-temperature peridotites, and concludes: "The

⁵ Bowen, Schairer, and Posnjak: This Journal, 26, 193-284, 1933; Bowen and Schairer, *ibid.*, 29, 151-217, 1935.

⁶ Honess, A. P., and Graeber, C. K.: Petrography of the mica peridotite dike at Dixonville, Pennsylvania, Penn. State Coll. Mining & Met. Exp. Sta., Bull. No. 2, 16 pp., 1926.

⁷ Daly, R. A.: Carbonate dikes of the Premier Diamond Mine, Transvaal, J. Geol., 33, 659-684, 1925.

⁸ Hess, H. H.: A primary ultramafic magma, Trans. Am. Geophys. Union, 18, Pt. I, 247-249, 1937.

Intrusion-temperature of Peridotites.

relatively low temperature of this peridotite magma is to account for, though its demonstrated high water-content probably the cause."

Bowen and Schairer⁹ have considered the similar peridotite and related mono-mineralic rocks, showing that an intrusion-temperature approaching 1900° C. would have been necessary to emplace some of them as dry melts. Such a temperature is impossibly high when the character of the contact metamorphism is considered. These authors hesitate, however, to admit the presence of the large amount of water that would be needed to lower the temperature of liquidity to something reasonable.

Everyone has been assuming that the intrusive rocks, in consideration were originally liquid magmas, either homogeneous liquids or liquids carrying crystals in suspension. The evidence on temperature makes such hypotheses improbable. The only remaining choice seems to be the hypothesis of plastic stiff mud. The ceramist is familiar with the fact that in the intrusion of clay mixes containing relatively little water, especially when certain organic chemicals are added that have a specific plasticizing effect. What is needed is, first, crystals of the right shape, and second, thin films of lubricating liquid separating these crystals, films sometimes only one molecular diameter in thickness. Such films, when composed of water or water solutions, can be heated far above the boiling point without developing enough vapor pressure to rupture rapidly.

It may be necessary, then, to give up our familiar concepts drawn from experience with flowing lavas, molten glass, fluid furnace slags, and go over to the concept of a magma of crystals lubricated by very thin films of a liquid which is not a silicate melt but is simply water or a water solution at a temperature far below the melting temperature of any constituent or system of constituents.

⁹ Bowen, N. L., and Schairer, J. F.: The problem of the intrusion in the light of the olivine diagram, Rept. XVI, Intern. Geol. Cong. Washington, pp. 391-396, 1936.

THE CRYSTALLOGRAPHY OF POTASSIUM TETRATHIONATE.

G. TUNELL, H. E. MERWIN, AND C. J. KSANDA.

ABSTRACT.

Analyzed artificial crystals of potassium tetrathionate have been investigated and their geometrical elements and optical constants have been determined; also, the dimensions of their structural unit cell and their space-group.

INTRODUCTION.

An attempt to correlate observations of the optical properties and angles of potassium tetrathionate crystals studied under the microscope, with the recorded properties of older crystals, brought to light discrepancies. This led to a reinvestigation of the crystallography of potassium tetrathionate, also to an X-ray determination of the unit cell dimensions and space-group. The crystals utilized by us were from several batches prepared by Dr. E. T. Allen in the Geophysical Laboratory. The method of preparation was as follows: To a sample of Wackenroder's solution (a mixture of thionic acids obtained by saturating sulphurous acid with hydrogen sulphide) potassium acetate was added and the liquid allowed to crystallize. The highest yield of tetrathionate was obtained from the middle fraction. This was separated from the lighter sulphate and pentathionate by a heavy liquid, bromoform and xylol, and finally recrystallized at room temperature from water containing several per cent of acetic acid. The chemical formula of the compound was checked by Doctor Allen as follows: 0.3009 g. of the compound was changed to K_2SO_4 and weighed; K_2SO_4 equivalent to 0.3017 g. of $K_2S_4O_6$ was found; 0.1023 g. of the compound was oxidized and the H_2SO_4 formed was precipitated as $BaSO_4$ and weighed; $BaSO_4$ equivalent to 0.1022 g. of $K_2S_4O_6$ was found.

MORPHOLOGY.

Crystals of potassium tetrathionate were pictured by C. F. Rammelsberg¹ as monoclinic prisms terminated by pyramids;

¹ These were erroneously supposed to be potassium pentathionate. Handbuch d. kryst.-physik. Chem., Wilhelm Engelmann, Leipzig, Abt. 1, pp. 495-496, 1881.

they were described by H. Baker² as hemimorph prisms terminated at one end by a pyramid and by a pinacoid; and described and pictured tridomitic monoclinic prisms with different up terminations. The crystals prepared by Doctor

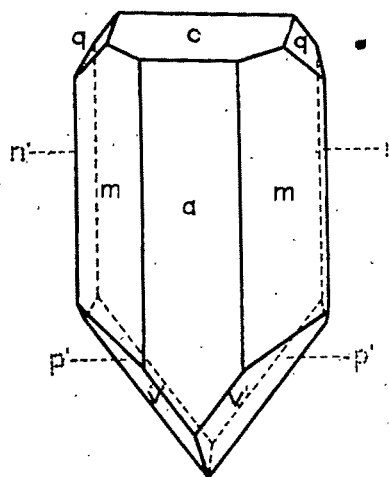
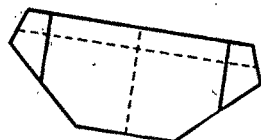


Fig. 1. Crystal of potassium tetrathionate measured with a goniometer.

those described by Fock. They have corresponding faces on both sides of a plane of symmetry; however, the faces required by an axis of symmetry are present on both sides of a pair required by an axis of symmetry. The faces are different in size or appearance if both are present. This is a drawing of one of the simplest crystals.

²J. Chem. Soc., 43, 354, 1883, in article by S. Shaw.

³Z. Kryst. Mineral., 19, 236-239, 1891. (Some details incorrect.)

The forms observed by us are⁴ $a\{100\}$, $a'\{100\}$, $b\{010\}$, $c\{001\}$, $l\{510\}$, $m\{320\}$, $m'\{320\}$, $n\{120\}$, $n'\{120\}$, $o\{211\}$, $o'\{211\}$, $p\{111\}$, $p'\{111\}$, $q\{011\}$, $q'\{011\}$, $r\{124\}$, $v\{111\}$, $v'\{111\}$. The form complementary to a is a' , etc.

Crystals were always prismatic to tabular with one end pyramidal and the other either entirely basal, or with the base diminished in the presence of a dome and pyramids. The front or the back pedion usually rested on the bottom of the crystallizing dish, in which case that face was large and the neighboring faces were narrow. If the surface of the liquid barely covered the crystals, both pedions were large, otherwise prism faces were large. In tufted groups crystals attached by the basal end grew much longer than those in the reverse position. In such groups, from a solution saturated with potassium sulphate and containing acetic acid, the front pedion was narrow and smooth, the back pedion indistinctly broad and rounded by stepping off toward the prism $\{510\}$; but in pure water solution the smooth front pedion was much wider than the back pedion together with the adjacent faces of $\{510\}$. The front form complementary to $\{510\}$ has not been observed. Both front and back pedions were present on all crystals. The side pinacoid was absent or exceedingly narrow. The prisms m and m' were both present and wide unless the crystals were very flat, and they appeared equally smooth and bright; the faces of prism n gave multiple signals from minute convexities, and under similar conditions were wider than the bright faces of prism n' . o' was usually absent, but when present it was minutely but distinctly striated parallel to a , while o was smooth or only obscurely striated. v' and p' terminated the lower end of the crystals, sometimes accompanied by q' or o' . r was observed only as an upper front form. Crystals dissolved in pure water and recrystallized under a capillary film of solution were flat and elongated and pointed similarly at both ends like holohedral orthorhombic crystals.

The numerical values of the geometrical elements were calculated from measurements made on a Goldschmidt two-circle goniometer. The angles for a small number of rather poor faces were not used. The coordinates, x' and y' , of the gnomonic face-pole of each of the other faces (x'/y' for prisms) were computed for each face and then combined to obtain the values of the projection elements, according to the method

⁴The correspondence of the letters used by the different authors to designate the forms is given in Table III.

TABLE I.
Measured and calculated ϕ and ρ angles of potassium tetrathionate.[†]

Letter	Gdt.	Symbol Miller	Calculated		Measured		Number of faces used	Limits	
			ϕ	ρ	ϕ	ρ		ϕ	ρ
<i>a</i>	$\infty 0$	100	90°00'	90°00'	90°00'	11	89°53' - 90°06'
<i>b</i>	0∞	010	0°00'	90°00'	0°06'	1
<i>c</i>	0	001	90°00'	14°01'	90°59'	14°00'	1*
<i>l'</i>	5∞	510	-74°55'	90°00'	-74°18'	4	-73°25' - -75°55'
<i>m</i>	$\frac{2}{3} \infty$	320	48°04'	90°00'	48°00'	27	47°41' - 48°09'
<i>n</i>	$\infty 2$	120	20°22'	90°00'	20°13'	17	19°13' - 20°30'
<i>q</i>	01	011	11°11'	52°08'	11°13'	51°59'	14	10°56' - 11°46'	51°00' - 52°15'
<i>p</i>	11	111	43°14'	60°00'	43°05'	59°56'	15	41°57' - 43°45'	59°40' - 60°08'
<i>o</i>	21	211	-52°09'	64°04'	-52°32'	64°08'	4	-52°18' - -52°56'	63°58' - 64°19'
<i>r</i>	$\frac{1}{2} \infty$	124	37°29'	38°29'	37°12'	38°35'	1
<i>v</i>	$\frac{1}{3} \infty$	111	-28°34'	55°09'	-28°35'	55°10'	12	-28°23' - -28°47'	54°50' - 55°20'

[†] Where both hemi-forms of a complementary pair were observed they have been included together in this table.
* A large but rough face on most crystals.

explained by V. Goldschmidt.⁶ The values of p_o' and q_o' obtained from the terminal faces were considered equally reliable and both were adjusted by means of the average value of p_o/q_o obtained from all these terminal faces and prisms, the sum ($p_o' + q_o'$) obtained from the terminal faces thus remaining unchanged. The polar and linear elements were then calculated from the projection elements. All calculations were carried out to the nearest tenth of a minute. In the tabulations the angles were finally rounded off to the nearest minute. Some of the limits of the measurements as recorded in Table I indicate considerable imperfection in the crystals, but as T. V. Barker⁷ has stated: "An important feature, peculiar to the Goldschmidt 'polar elements,' is that they are adapted to the derivation of very accurate constants, for all the measured angles can be taken into account." Thus the calculated and the averaged measured angles are but a few minutes apart.

The earlier measurements by Rammelsberg¹ and by Fock⁸ were made on one-circle goniometers, which fact must be considered in relation to the accuracy of the elements⁷ calculated by them, and the interchanges of angles, and other inconsistencies in their publications.

Our geometrical elements are compared with those of Rammelsberg and of Fock in Table II. Those of Rammels-

TABLE II.

Linear and polar elements of potassium tetrathionate.

Tunell, Merwin, and Ksanda

$$\begin{aligned} a:b:c &= 1.3885:1:1.2615, \quad \beta = 104^\circ 01', \\ p_o:q_o:r_o &= 0.9085:1.2240:1, \quad \mu = 75^\circ 59', \\ p_o' &= 0.9364, \quad q_o' = 1.2615, \quad r_o' = 0.2495. \end{aligned}$$

Fock

$$\begin{aligned} a:b:c &= 1.3952:1:1.2666, \quad \beta = 104^\circ 16'. \text{ (Recalculated by Tunell, Merwin,} \\ &\text{and Ksanda from the three angles taken by Fock as fundamental, namely,} \\ q:q \text{ [Fock's letters]} &= 101^\circ 40', \quad m:a = 42^\circ 02', \text{ and } c:a = 75^\circ 44'. \end{aligned}$$

Rammelsberg

$$\begin{aligned} a:b:c &= 1.4099:1:1.2641, \quad \beta = 104^\circ 32'. \text{ (Recalculated by Tunell, Merwin,} \\ &\text{and Ksanda from the three angles taken by Rammelsberg as fundamental,} \\ &\text{namely, } o:o \text{ [Rammelsberg's letters]} = 67^\circ 48', \quad o':o' = 78^\circ 22', \text{ and } o' = \\ &53^\circ 40'. \end{aligned}$$

⁶ Z. Kryst. Mineral., 30, 272-294, 1898.

⁸ Graphical and Tabular Methods in Crystallography, Thomas Murby, and Company, London, p. 94, 1922.

⁷ Barker's opinion (see Op. cit., p. 16); that the readings of two-circle goniometry are more faithful to the crystal in its entirety than those of one-circle goniometry seems to us to be justified.

berg are not entirely consistent with his three fundamental angles. The values recalculated by us from these angles are: $a':b':c' = 0.9285:1:1.2641$, $a'c' = 78^\circ 28'$. The values given by Rammelsberg are: $a':b':c' = 0.9285:1:1.264$, $a'c' = 78^\circ 45'$. Fock recalculated Rammelsberg's values as: $a':b':c' = 0.9285:1:1.2642$, $a'c' = 78^\circ 28'$. Thirteen of the angles calculated by Rammelsberg are also in error by a few minutes. They are listed here with his letters, and with the letters of Tunell, Merwin, and Ksanda: oo' or op' , mm or vv , $m'm'$ or qq , mm' or vq , mm' or vq' , ${}^3p^3p$ or nn , a or an , p or mn , $\frac{r}{3} a$ or ca , m or $a'v$, m' or aq , om or ov , $o'm'$ or pq .

The values of these calculated angles with the arithmetical errors corrected are given in Table V. Rammelsberg's assignment of symbols was consistent.

The values calculated by us from Fock's three fundamental angles are: $a'':b'':c'' = 0.93014:1:1.26664$, $a''c'' = 75^\circ 44'$, the values given by Fock are $a'':b'':c'' = 0.93017:1:1.26664$, $a''c'' = 75^\circ 44'$. Fock selected as his basal pinacoid the face designated by Rammelsberg as $\frac{r'}{3}$. Fock says: "Die Aufstellung der Krystalle wurde aus leicht ersichtlichen Gründen etwas anders gewählt. Das Hemidöma $c\{103\}$ wurde zur Basis $\{001\}$, die prismatischen Formen dagegen unverändert beibehalten." Fock selected as his three fundamental angles the measured angles: $am = 42^\circ 02'$, $ac = 75^\circ 44'$, $qq = 101^\circ 40'$. In accordance with the quotation given above, he assigned Miller indices to these forms as follows (Fock's letters): a , $\{100\}$; m , $\{110\}$; c , $\{001\}$; q , $\{011\}$. This assignment of course determines the indices of all the other forms. Fock's derivations of the Miller indices of his three pyramids, o , p , and v (Fock's letters), are all erroneous. For these forms he gave the indices: o , $\{111\}$; v , $\{133\}$; p , $\{111\}$; the correct indices of these forms with Fock's choice of axes and unit forms are: o , $\{433\}$; v , $\{233\}$; p , $\{233\}$. Fock's calculated angles, oo , pp , vv , ao , av , ap , are also in error; the correct values of these calculated angles are given in Table V. In addition to the mistakes already mentioned, Fock interchanged his measured angle oo with his measured angle pp , and likewise his measured angle ao with his measured angle ap .

In his paper Fock quoted Rammelsberg's measured angles and corrected some mistakes in Rammelsberg's computations.

However, Fock interchanged Rammelsberg's measured angles oo and pp (Fock's letters), but the remainder of Rammelsberg's measured angles quoted by Fock are given correctly. Fock recalculated part of Rammelsberg's calculated angles. The values recalculated by Fock for the following calculated angles are correct to $\pm 1'$ (Fock's letters) : vv , qq , am , ca , ao , av , aq ; but for the angle an there is an error of several minutes. The large discrepancy between the values of oo as measured and published by Rammelsberg and as measured by Fock, and likewise between the values of pp , ao , and ap , measured by Rammelsberg and by Fock (cf. the writers' Table V), is due to the fact that Fock interchanged his measured angles relating to o and p which in his drawing, and according to his Miller symbols, are an upper back or lower front pyramid and an upper front or lower back pyramid respectively. Such an interchange of angles and wrong assignment of indices are much less likely to occur with the use of the two-circle goniometer and the gnomonic projection than with the use of the one-circle goniometer and stereographic projection.

The correspondence of the forms observed by Rammelsberg, by Fock, and by us is shown in Table III. Our choice of axes and unit forms is not entirely the same as that of Rammelsberg or that of Fock. The transformation matrices are assembled in Table IV.

TABLE III.

Correlation of the letters used by the various authors.

Tunell, Merwin, and Ksanda	Fock	Rammelsberg
a & a'	a	a
b		
c	c	$r'/3$
l'		
m & m'	m	p
n & n'		sp
q & q'	q	m'
p & p'	p	o'
o & o'	o	o
r		
v & v'	v	m

DETERMINATION OF THE STRUCTURAL UNIT CELL AND SPACE-GROUP.

X-ray analysis shows that the morphological ratio of a to b must be doubled for structural purposes but confirms the

TABLE IV.
Transformation matrices.*

From \ To		Rammelsberg 1881	Fock 1891	Tunell, Merwin, and Ksanda (Morphological) 1938	Tunell, Merwin, and Ksanda (Structural) 1938
Rammelsberg	$\left\{ \begin{array}{l} 1\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$		$\left\{ \begin{array}{l} 1\ 0\ \frac{1}{2} \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} \frac{1}{2}\ 0\ \frac{1}{2} \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 3\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$
Fock	$\left\{ \begin{array}{l} 1\ 0\ \frac{1}{2} \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 1\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$		$\left\{ \begin{array}{l} \frac{1}{2}\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 3\ 0\ 1 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$
Tunell, Merwin, and Ksanda (Morphological)	$\left\{ \begin{array}{l} \frac{1}{2}\ 0\ \frac{1}{2} \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} \frac{1}{2}\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 1\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$		$\left\{ \begin{array}{l} 2\ 0\ 1 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$
Tunell, Merwin, and Ksanda (Structural)	$\left\{ \begin{array}{l} \frac{1}{2}\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 1\ 0\ \frac{1}{2} \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} \frac{1}{2}\ 0\ \frac{1}{2} \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} \frac{1}{2}\ 0\ \frac{1}{2} \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 1\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{array} \right.$

* For the method of using these transformation matrices, see Barker, T. V.: *Systematic Crystallography*, Thomas Murby & Co., London, pp. 32--34, 1930; or Donnay, J. D. H.: *Am. Mineral.*, 22, 621-624, 1937; for the reason for the fractional form see Peacock, M. A.: *Am. Mineral.*, 23, 38, 1938.

morphological ratio of c to b . While the X-ray results would permit the same choice of the base as that made in Fock's and in our morphological study, this choice would not give a unit cell in which the glide directions are oriented in conformity with the conventions of the *International Tables for the Determination of Crystal Structures*. Therefore for the sake of conformity with the conventions of those tables, the plane chosen by Rammelsberg as his base was taken as 001 in the röntgenographic study. The unit cell dimensions and systematically missing spectra were determined by means of rotation and Weissenberg photographs taken with the crystals rotating about the c - and b -axes.⁸ Equator and first and second layer-line

* The crystals of potassium tetrathionate are mostly elongated parallel to the c -axis. In order to obtain a suitable specimen for rotation about the b -axis, a crystal was severed roughly parallel to the base, and one end with suitable faces for orientation was utilized. The cutting of the crystal in a definite direction was readily accomplished by means of a small apparatus described by F. E. Wright (*Min. Mag.*, 23, 157-158, 1932). In using this

TABLE V.

Interfacial angles of potassium tetrathionate.

Interfacial angles		Rammelsberg		Fock		Tunell, Merwin, & Ksanda Calculated
		Measured #	Recalculated†	Measured	Recalculated‡	
oo	Z11 \wedge Z11	67°48'	*	78°31'§	67°17'	66°59'
pp	111 \wedge 111	78°22'	*	67°50'§	78°19'	78°14'
op	Z11 \wedge 111	81°05'	81°00'			81°37'
op'	Z11 \wedge 111	56°30'	56°43'			56°36'
vv	111 \wedge 111	92°45'	92°53'	92°19'	92°35'	92°14'
qq	011 \wedge 011	101°38'	101°29'	101°40'	*	101°31'
vq	111 \wedge 011	32°00'	31°37'			31°55'
vq'	111 \wedge 011		74°18'			74°29'
mm	320 \wedge 320	84°18'	84°36'			83°51'
ma	320 \wedge 100	42°15'	42°18'	42°02'	*	41°56'
mi	120 \wedge 120		139°45'			139°17'
na	120 \wedge 100	70°06'	69°53'			69°38'
mn	320 \wedge 120	28°07'	27°35'			27°43'
ca	001 \wedge 100	75°25'	75°28'	75°44'	*	75°59'
a'o	100 \wedge Z11	45°30'	45°20'	53°36'‡	44°54'	44°46'
a'v	100 \wedge 111	67°20'	67°31'	67°08'	67°05'	66°54'
ap	100 \wedge 111	53°40'	*	45°03'‡	53°34'	53°37'
aq	100 \wedge 011	80°48'	80°52'	81°07'	81°03'	81°11'
ov	Z11 \wedge 111	21°45'	22°11'			22°08'
pq	111 \wedge 011	27°16'	27°12'			27°34'
m'q	320 \wedge 011			66°13'	66°12'	66°12'
mq	320 \wedge 011			50°41'	50°36'	50°51'

|| Letters of Tunell, Merwin, and Ksanda.

The angles in this column are the supplements of the measured angles reported by Rammelsberg.

† Recalculated by Tunell, Merwin, and Ksanda from the three measured angles chosen as fundamental by Rammelsberg or by Fock respectively. The fundamental angles are indicated by asterisks.

§, ‡ The angles in each of these pairs must have been interchanged by Fock.

Weissenberg resolutions were made about the *c*-axis, and an equator Weissenberg resolution was made about the *b*-axis. The unit cell dimensions, all determined by purely röntgenographic measurements are: $a_0 = 22.05$ Å, $b_0 = 7.99$ Å, $c_0 = 10.09$ Å, all ± 0.02 Å, $\beta = 102^\circ 05' \pm 15'$. Diffraction effects

apparatus the present writers have found it extremely helpful to support the crystal on a thin layer of plasticine. Even very brittle crystals such as calaverite, which, without the supporting layer of plasticine, fly to bits at the touch of the cutting blade, can be cut in desired directions when so supported.

were obtained from the following planes: $g00$, $0g0$, $00g$, $0gu$, $0gg$, $g0g$, $uu0$, $gg0$, uuu , uug , ggg , where g denotes any even number and u denotes any odd number. No diffraction effects were obtained from the following, although representatives of each were in a position to diffract during the exposures of the Weissenberg photographs: $u00$, $0u0$, $00u$, $0uu$, $0ug$, $u0u$, $u0g$, $g0u$, $ug0$, $gu0$, ugu , ugg , guu , gug . These missing spectra are characteristic of the space-groups $C_{2h}^0 - C2/c$ and $C_s^4 - Cc$. As already mentioned, the morphology of the potassium tetrathionate crystals affords a strong indication that they belong to the crystal class $C_s - m$. That the symmetry of potassium tetrathionate is lower than holohedral was conclusively established by tests for pyroelectric and piezoelectric effects, both of which were proved to be present.⁹ Potassium tetrathionate therefore belongs to the space-group $C_s^4 - Cc$.

The density of potassium tetrathionate was determined to be 2.296 by Hertlein,¹⁰ using a flotation method. The unit cell accordingly contains 8 molecules of $K_2S_4O_{10}$, the density calculated from the X-ray measurements on this assumption being 2.296, in exact agreement with the measured density.

A comparison of the axial ratios obtained from the röntgenographic measurements with those obtained from the morphological measurements is given in Table VI.

TABLE VI.

Crystallographic elements referred to the structural axes.

a	b	c	β	
2.760	1	1.263	$102^\circ 05'$	Tunell, Merwin, and Ksanda (röntgenographic)
2.7581	1	1.2615	$102^\circ 20'$	Tunell, Merwin, and Ksanda (morphological)
2.7656	1	1.2666	$102^\circ 05'$	Fock* (morphological)
2.7855	1	1.2641	$101^\circ 32'$	Rammelsberg* (morphological)

* Recalculated by Tunell, Merwin, and Ksanda.

In order to facilitate future identification of potassium tetrathionate by the X-ray powder method, the planar spacings and relative intensities of the lines in a powder photograph taken with Cu-radiation filtered through nickel foil are recorded in Table VII.

* The authors are indebted to Messrs. S. B. Hendricks and M. E. Jefferson of the U. S. Department of Agriculture, Bureau of Chemistry and Soils, for their kindness in testing the crystals for pyro- and piezoelectric effects.

¹⁰ Hertlein, H.: Z. phys. Chem., 19, 297, 1896.

TABLE VII.

Planar spacings and relative intensities of the X-ray diffraction lines of $K_2S_4O_6$ from a powder spectrum taken with filtered Cu-K radiation.

Line	Intensity observed*	d/n
1	2	9.48
2	3	6.21
3	3	5.80
4	5	5.387
5	3	4.946
6	4	4.436
7	3	4.005
8	1	3.830
9	3	3.607
10	10	3.371
11	7	3.173
12	7	3.095
13	8	2.921
14	6	2.694
15	4	2.529
16	2	2.454
17	4	2.391
18	3	2.299
19	1	2.267
20	6	2.158
21	4	2.097
22	2	2.029
23	4	1.947
24	5	1.908
25	4	1.819
26	5	1.801
27	4	1.777
28	3	1.717
29	4	1.678
30	3	1.634
31	5	1.594
32	2	1.550
33	3	1.518
34	1	1.492
35	4	1.453
36	6	1.415
37	1	1.361
38	1	1.344
39	4	1.328
40	5	1.290
41	1	1.264
42	5	1.247
43	5	1.227
44	3	1.196
45	2	1.172
46	3	1.149
47	2	1.130
48	3	1.113
49	4	1.080
50	5	.990
51	3	.946
52	4	.898

* Estimated intensities of the diffraction lines are based on a scale of ten, where ten represents the intensity of the strongest line.

CLEAVAGE, REFRACTIVE INDICES, DISPERSION, OPTICAL
ORIENTATION.

The monoclinic crystals, elongated parallel to the c -axis, have a perfect cleavage parallel to 100. The optic axial plane is 010; $\gamma \wedge c = 33^\circ_{\text{O}}$ and 34°_{F} in the obtuse angle β . $2V$, positive, $= 66^\circ_{\text{O}}$ and 69°_{F} . An optic axis emerges in air $38\frac{1}{2}^\circ_{\text{O}}$ and 36°_{F} from the normal to the cleavage, in the obtuse angle β .¹¹

TABLE VIII.
Dispersion of refractive indices.*

	α $\pm .0002$	β $\pm .0002$	γ $\pm .0002$
404' Hg	1.6160	1.6370	(1.6791)
G'	1.6089	1.6285	1.6695
436 Hg	1.6085	1.6281	1.6690
F	1.5999	1.6180	1.6575
501 He	1.5979	1.6156	1.6548
546 Hg	1.5931	1.6098	1.6483
588 He	1.5897	1.6058	1.6436
D	1.5896	1.6057	1.6435
C	1.5856	1.6009	1.6382
668 He	1.5849	1.6001	1.6374
706 He	1.5832	1.5981	1.6352

* Measurements for helium and mercury lines by minimum deviation. Interpolated for the letters and for the value in parentheses.

¹¹ According to Fock, about 48° in the acute angle between the a - and c -axes (designated by Fock the acute angle β).

AN IMPROVED TORSION GRAVITY METER.

F. E. WRIGHT AND J. L. ENGLAND.

ABSTRACT.

In the improved instrument, recently built at the Geophysical Laboratory, the torsion element is the same as that used heretofore, but its other parts have been rearranged to provide simpler control for operation in the field. The present apparatus is lighter than its predecessor and gives promise of even better field performance. The last instrument, during one period of eight months' service in 1937 in occupying and reoccupying old and new gravity stations, yielded results that, for any given station, agreed within one milligal. The new instrument is mounted inside a covered, insulated motor truck. Under ordinary conditions twenty stations or more per day can be occupied. The torsion element in this balance is under load only during the time required to make a gravity measurement (either 4 or 6 minutes); otherwise it is at rest and the small residual strains are dissipated. This procedure maintains the characteristics of the spring remarkably constant.

Experiments and tests with torsion gravity meters have been made at the Geophysical Laboratory for a number of years. In 1930 a gravity balance was constructed that has proved quite successful in field use. For one period of eight months in 1937 during which many stations were occupied repeatedly, the values obtained for any given station agreed within one part in a million (± 1 milligal). Laboratory study has yielded much information on the elastic behavior of various materials and on the factors that affect the accuracy of the readings of the instrument.

In the light of these experiences an improved instrument, based on the type of elastic system originally adopted, has recently been built in the Laboratory and been found to be better adapted to field use than its predecessors; it weighs less, is more effectively insulated, and is of sturdier construction.

Its torsion element consists of a helical spring of fine, well annealed tungsten wire; it is mounted at its two ends to a horizontal rotating frame and tapers from the ends to the center at which a cross-boom is attached with a small mass of platinum at its outer end. The measurement is made by rotating the frame first in a clockwise direction, thereby winding the spring, which in turn raises the cross-boom against gravity to a horizontal position. The greater the weight or gravitational attraction on the platinum mass at the end of the boom the larger the number of turns of the frame required to raise the boom

to its horizontal position, at which the reading on the graduated circle attached to the frame is recorded. The frame is then rotated counterwise, the boom is lowered gradually, passes through its original hanging position of rest, and is then slowly raised to the horizontal position on the left side. The angular rotation of the supporting frame required for the boom to pass from the first horizontal position to the second is the measure of the relative value of gravity at the station as compared with that of another station previously occupied.

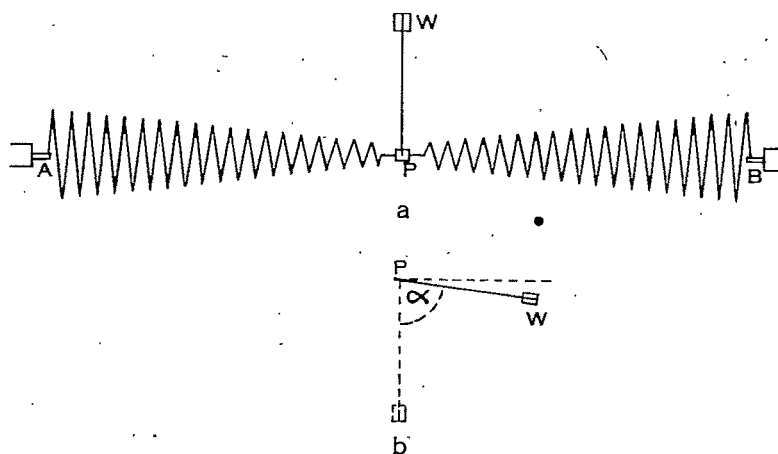


Fig. 1. (a) Schematic plan of helix spring and cross-boom, PW . (b) Diagram of vertical section through boom PW , which includes an angle α with the vertical. The horizontal direction is indicated by the dotted line.

The positions of horizontality are chosen because they are near the upsetting positions of the boom (3° or less) where a small angular rotation of the frame produces a large movement of the boom and where the vibration of the elastic system is non-harmonic. The elastic system as a whole is astatic and self-damping to such a degree that all elastic vibrations are quickly eliminated. The boom near its upsetting position and the tapering form of the helical springs are features that decrease resonance of the oscillating boom to disturbances of any frequency.

The forces acting on the boom near the horizontal position are easily computed. In Fig. 1a the spring with cross-boom is shown schematically in plan; its ends are attached to the supporting frame at A and B ; the cross-boom is attached at the

center P and carries a small weight W at its outer end. Figure 1b is a vertical section showing the boom near the horizontal position. W is the center of gravity of the arm PW of length r ; the arm includes the angle, α , with the vertical.

Let K be the moment necessary to rotate (including bending) unit length (1 cm.) of the torsion wire through unit angle (one radian); and l , the length of the torsion wire on each side of the boom. The total torsional moment is then $\frac{2K}{l} (\theta - \alpha)$ where θ is the angle (in radians) of rotation of the frame supporting the spring.

The moment due to gravity pull on the boom is $-mgr \sin \alpha$. At the position of rest the moment due to gravity is exactly counterbalanced by the moment of torsion; therefore

$$mgr \sin \alpha = \frac{2K}{l} (\theta - \alpha) \quad (1)$$

or

$$mg \sin \alpha = C (\theta - \alpha) \quad (2)$$

wherein

$$\frac{2K}{r.l} = C$$

From this equation the behavior of the system can be ascertained for different positions of the arm (α), for different values of the mass (m) and of gravity (g) and for different angles of rotation (θ) of the frame. Thus for $\alpha = \frac{\pi}{2}$ equation

(2) reads $mg = C \left(\theta - \frac{\pi}{2} \right)$, a linear relation between g and θ .

If the weight, mg , be held constant, we obtain on writing $\frac{mg}{C} = C'$ the equations

$$\theta = C' \sin \alpha + \alpha \quad (3)$$

$$\frac{d\theta}{d\alpha} = C' \cos \alpha + 1 \quad (4)$$

$$\frac{d^2\theta}{d\alpha^2} = -C' \sin \alpha \quad (5)$$

In equation (3) we have for $\alpha = 0$, $\theta = 0$; for $\alpha = \frac{\pi}{2}$, $\theta = \frac{\pi}{2} + C'$ and $\frac{d\theta}{d\alpha} = 1$ (equation 4). For $\alpha > \frac{\pi}{2}$, $\cos \alpha$ is negative and the value of $\frac{d\theta}{d\alpha}$ decreases and vanishes for $C' \cos \alpha + 1 = 0$ or $C' = -\frac{1}{\cos \alpha}$. At this point the system is unstable and an infinitesimal increase in θ produces a very large change in α . For this upsetting point we have from equation (3)

$$\theta = -\tan \alpha + \alpha \quad (6)$$

an equation that can be satisfied for any value of θ greater than π ; thus for $\alpha = \pi$, $\theta = \pi$; for $\alpha = \frac{\pi}{2}$, $\theta = \infty$. The important feature to be noted is that by use of an elastic system such that θ is large, the upsetting point is near the horizontal position of the boom and a high degree of sensitivity is obtained. In the gravity measuring instruments built in the Geophysical Laboratory the graduated circles read with vernier to $10''$ of arc; in order that the instrument read directly to one part in a million the angle θ should be at least $10'' \times 10^6 = 2777.78^\circ$; therefore an angular rotation of approximately 1400° of the frame is required to raise the boom from its vertical position of rest to the horizontal position. In this case the boom upsets at $\alpha = 92^\circ 32'$, or roughly $2\frac{1}{2}^\circ$ above its horizontal position.

To insure an accuracy of one part in a million or better, certain precautions should be taken. The elastic system should be under load only during either 4 or 6 minutes required to make the necessary measurements at a station. By introducing stresses into the system first in one direction and then in the opposite direction the successive strains thereby set up are in opposite directions and tend to counteract each other, so that at the end of the short exposure only small residual strains remain. Between stations the helical spring is held at rest, supported by suitable pans with the boom at rest in the hanging vertical position and clamped so that it does not move. During the periods of rest the small residual strains are dissipated and the spring returns to its original unstrained state. There is good evidence that elastic after-effects or hysteresis

are largely of the nature of surface phenomena, and that both the outer surface and the surfaces between individual crystals in a crystalline aggregate are involved.

To obtain reproducible results it is necessary that at each station a definite time schedule of operations be strictly followed in order that the elastic and other properties of the spring be kept constant. Elastic hysteresis sets in immediately after a load is applied to the spring. Hooke's law is valid only to approximately one part in 10,000. The elastic hysteresis effect is roughly exponential in character and enters into any elastic system under load and increases with the load. Therefore in an elastic system intended to be used for the measurement of gravity to one part in a million or better, it is wise for the observer to introduce as small loads as possible, and to recognize that the elastic response is imperfect and that the deformation is dependent on the rate at which the spring is loaded and unloaded; also to maintain the elastic system free from load except during the short measuring periods.

The temperature of the spring should be held constant to 0.02° C. and all measurements should be made at the same temperature; otherwise the elastic response changes and introduces an uncertainty into the result that cannot be completely controlled by use of a correction factor especially if the elastic system is under continuous load. It has long been known that the deformation response of an elastic system to an applied load of fixed amount depends on the previous treatment of the system. For this reason a disturbing factor is avoided by maintenance of constant temperature. In the present instrument this is attained either by surrounding the instrument with ice or by use of an electrically controlled thermostat.

The air pressure inside the instrument should be held constant and preferably at 1 or 2 mm. of mercury. A change in pressure of 4 to 5 millimeters air pressure decreases the gravity reading by one milligal.

The air in the instrument should be kept dry by use of a suitable drying agent.

The instrument should be equipped with accurate levels, reading to $20''$ of arc, to enable the observer to level the instrument accurately in both lengthwise and crosswise directions.

For convenience and speed of operation the instrument may well be transported in a motor truck with insulated walls and so carried that at a gravity station it can easily be transferred to

a heavy tripod resting on the ground and reaching into the truck through holes in the floor. With this arrangement the apparatus is not exposed to rapid changes in outside temperature and to inclement weather. In actual transport the gravity meter rests on an inflated inner tube of an automobile tire to reduce the jolts and jars of transportation.

The shell of the new gravity balance is made of an aluminum alloy of high mechanical strength; it is shown in vertical section in Fig. 2. Its walls are sufficiently thick to permit without deformation a reduced inner air pressure of 1 mm. of mercury. It comprises a forward tubular section with an outwardly

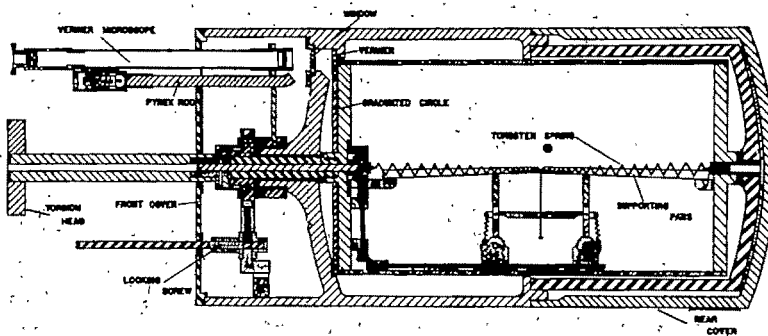


Fig. 2. Vertical section through gravity balance.

domed transverse wall, and a similarly domed rear cap that fits tightly into it. To the same end of the section a yoke is secured, which is axially bored to receive the rear axis of the rotating frame that supports the helix. The front axis of this frame rests in the axial bore of the transverse wall.

To the front end of the rotating frame a graduated circle is attached; the vernier is secured to the housing. The circle and vernier are mounted inside the shell in order to obtain a more satisfactory support for the circle than has heretofore been possible, and to insure better thermal insulation. The graduations on the circle and vernier are viewed through a low-power microscope mounted outside the vacuum chamber on a rotatable arm so that any part of the vernier can be brought into the field. The circle is illuminated by a small electric bulb whose rays are transmitted through a rod of Pyrex glass or fused silica and a small plate glass seal of arcuate shape.

The rotating frame is a sturdy casting to insure absence of flexure. Attached to the inner surface of one side of this frame is the gear mechanism for raising the pans that support the helix when at rest; also thin S-shaped springs of flat phosphor bronze for holding the cross-boom of the spring against movement. The gear system is used in place of the flexible wire heretofore employed; the gears are operated from the outside by a rod that passes through the forward axle of the frame, as indicated in Fig. 2. The device for clamping the fine adjustment tangent screw is also shown in Fig. 2; the tapered end of the locking screw bears against the beveled end surface of a plunger and forces it forward to press against the friction plate.

The forward end of the housing is capped by a snugly fitting cover to prevent moisture from entering the enclosed, but not evacuated space. In this space several parts are mounted as shown in Fig. 3, which is a photograph of the forward end of the apparatus with the front cover removed.

The two microscopes for observing the end of the boom are seen in Fig. 3 on opposite sides of the cylindrical housing. The optical system of each microscope comprises two parts; an inner part consisting of a right angle prism (Fig. 4) and an objective lens which forms an image of a fine glass filament, attached to the end of the boom, on a reticle etched on the plane surface of a lens mounted 2 mm. in front of the plate glass window which serves as seal for the vacuum; these elements are mounted rigidly on recesses in the housing. The outer part is mounted in a tube (Fig. 3), and consists of an objective lens which images both the reticle and the image of the glass filament in the focal plane of the eyepiece. This disposition of the optical system was adopted to insure absence of movement of its parts, especially of the inner portion.

The glass filament mentioned above is one mil. (0.025 mm.) thick and is attached to a short piece of wire at the end of the cross-boom (Fig. 4). The filament extends parallel with the axis of rotation of the helix and its supporting frame; it is illuminated by a small electric bulb placed in front of the eyepiece of the microscope on the side opposite to that of the boom: the rays from the bulb pass through the microscope system and across the cylinder space to the glass filament which has the appearance, in transmitted light, of a narrow bright band between two black bars. The diameter of the filament is such that the light band is but slightly wider than the cross hair of

the reticle, thus enabling the observer to make accurate settings. When the boom is on the opposite side the situation is reversed. A second glass filament, also attached to the boom and parallel with the first, is then viewed under conditions analogous to those of the first. The two glass filaments are used to offset



Fig. 3. Photograph of forward end of gravity balance. Front cover has been removed.

the sag in the helix, to provide satisfactory signals, and to facilitate the adjustment of the instrument. Experience with various devices has proved that this method is the most satisfactory thus far tested. It was first used on the gravity balance of 1930.

The temperature inside the vacuum chamber of the housing

is measured at each station by two special mercurial thermometers reading to 0.01° C. and mounted on the inner surface of the rotating frame. Each thermometer is illuminated by the method used for the cross-boom signals; the thermometer scale is brought into focus by means of a negative lens set in the rotating frame on the side opposite to that of the thermometer. The effect of this lens when placed in front of the objective of the

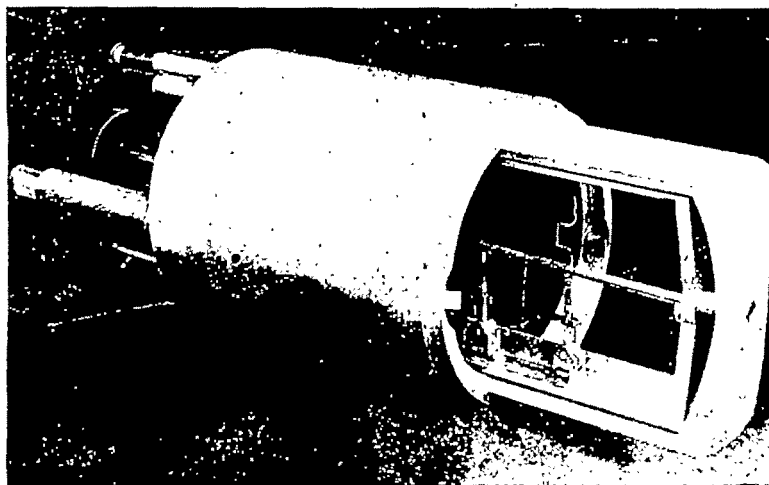


Fig. 4. Photograph of rear end of gravity balance with rear cover removed.

observing microscope is to increase its focal length so that the thermometer is imaged on the reticle rather than the glass filament of the helix boom which is held at rest during these readings by the supporting pans and clamps.

The reduced air pressure in the inner chamber of the housing is measured by means of a small mercury manometer mounted on the front panel of the apparatus. The air is kept dry by use of calcium chloride.

The instrument is leveled by means of screws in the metal table of the tripod on which the instrument is placed at each gravity station. The levels are "Zeiss" theodolite levels and read directly to $20''$ of arc. They are mounted in the forward space of the housing (Fig. 3). They are viewed through a low-power lens so mounted that both levels, showing the longitudinal and transverse tilts respectively, are in the field of view.

They are illuminated by a small electric bulb whose rays are transmitted to them through a mounted Pyrex rod.

The protective housing of the apparatus is built of a series of concentric cylinders of stainless steel. The outer shell rests in, and is secured to, a cradle by clamp rods that are drawn down on shock-absorbing strips of sponge rubber resting on the upper half of the cylinder. The cradle rests on leveling screws that reach through the metal table of a heavy tripod whose legs extend through holes in the floor of the truck to the ground. During transportation the gravity balance is shifted to a platform that rests on the inflated inner tube of an automobile tire and is held in place by springs attached to the truck. Other springs hold the instrument in place on the platform. The protective housing has a thick layer of insulating material (balsa wood) between the outer shell and the second shell and the end pieces. These compartments surround an inner space that is water tight and contains either ice or an electrically controlled thermostat for maintaining constant temperature within the helix chamber.

During occupation of a gravity station the time for the schedule of operations is communicated to the observer through a telephone headset from a clock beating seconds and sending a signal at 50 seconds and on the minute.

Extensive series of routine measurements with the new gravity balance have not yet been made. With its predecessor, however, many series of tests have been carried out during the past eight years. Difficulties have arisen at times and much effort has been spent in ascertaining their causes and in eliminating them. Ordinarily the cause has been of a mechanical kind, such as the slight shift of an optical element, rather than imperfect response of the elastic element itself.

The faithful behavior of the elastic systems tested during this investigation has been a source of wonder to the observers. The behavior of an elastic element at any given time depends of course upon its previous treatment; at no time is it perfectly elastic; the hysteresis curve of deformation, which it follows under a given load, is determined quite exactly by its previous history; in other words, by the amount and distribution of stresses which it harbors at the given moment. If these stresses and resultant strains are large and non-uniform, its elastic behavior is erratic and unreliable. On the other hand, if the elastic element has been properly annealed and well seasoned

and is maintained in that state, its response to a given small load is so constant, month after month, that measurements accurate to one part in a million or better are possible.

Special study has been made of the character of the curves of deformation followed by springs of tungsten and other materials, including single crystals, under load and their recovery therefrom. Many series of runs have been made in the Laboratory covering different time-periods from minutes to days and information has been gathered on the nature of elastic after-effects when measured with high accuracy.

Experience has proved that with proper treatment a spring maintains its characteristics remarkably well with no appreciable change in its behavior for long periods of time; and, that, as a result, no detectable shift arises in what would be called the zero point in other instruments. With careful handling and exact observance of a definite time schedule during the actual measuring periods and with freedom from load between these periods the spring preserves its state so satisfactorily that it can be relied upon to give reproducible results accurate to one part in a million. Its behavior under applied load is, however, not that of a perfectly elastic body but one in which certain departures from Hooke's law enter to modify the elastic response and to introduce a time element into rate of deformation that must be recognized, if the desired accuracy is to be attained. The realization of this condition led in 1923 to the adoption of the principle of the method followed in the series of gravity balances that have been constructed in the Geophysical Laboratory. The results obtained with these instruments have demonstrated the validity of the principle and have yielded valuable data on the deformation of certain materials when subjected to loads well within their elastic limit.

THE CONCENTRATION OF THE LESS FAMILIAR ELEMENTS THROUGH IGNEOUS AND RELATED ACTIVITY.*

E. G. ZIES.

ABSTRACT.

The bulk of the Earth's crust is composed of igneous rocks and with respect to its entirety the concentration of the less familiar elements is extremely low. They assume economic importance only when they have been reconcentrated in some favorable physico-chemical environment. Some attain this importance when through the various processes of magmatic differentiation they have accumulated in the mother liquor from which the pegmatites are derived and combine with other elements to form distinct minerals. It is quite probable that acid vapors are important at this stage of differentiation because the halides, sulphides, and even oxides of many of these elements are volatile at the prevailing temperatures. Considerable evidence has been obtained that this type of concentration also takes place during volcanic activity. There is still another method by which a rare element can accumulate in a favorable environment. It can be segregated within the crystal lattice of some common mineral because its ionic radius is almost identical with that of one of the constituents in the mineral. This theory of "camouflage" was developed by V. M. Goldschmidt and is a useful guide for the analyst in searching for the rare and less familiar elements.

Throughout the ages mankind has been striving to increase the usefulness of the tools which he uses for providing himself with sustenance, with greater creature comforts, and with weapons of offense and defense. The archaeologist designates the great historical periods as the stone age, the bronze age, and the iron age, and implies thereby an increase in man's ability to use available materials in the making of his artifacts. We are now living in an age which can no longer be designated with the name of any single material. It is true that the present may still be called the iron age, nevertheless aluminum has become a potent factor in gradually lessening the dominance of iron. Aluminum is even more abundant in the Earth's crust than iron and has the desirable property of lightness. Its utilization was delayed until a method was found for obtaining it in a high degree of purity from its ores. This has been accomplished only within the last forty years.

The present age, with its emphasis on speed, demands that the materials used in the construction of its artifacts shall be

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produced at low cost and shall possess lightness and resistance to deformation and corrosion. In the effort to secure these properties, the chemist is encouraged to study more intensively the chemical and physical properties of elements which are less common in the Earth's crust than iron and aluminum. One outstanding result of this effort is the addition of magnesium

TABLE I.
Average Composition of Igneous Rocks.
Major and common elements.¹

	1	2	3	4
Oxygen	46.59	46.41	47.29	47.2
Silicon	27.72	27.58	28.02	28.0
Aluminum	8.13	8.08	7.96	8.0
Iron	5.01	5.08	4.56	4.5
Calcium	3.63	3.61	3.47	3.5
Sodium	2.85	2.83	2.50	2.5
Potassium	2.60	2.58	2.47	2.5
Magnesium	2.09	2.09	2.29	2.5
Titanium63	.720	.46	.33
Phosphorus13	.157	.13	.22
Hydrogen13	.129	.16	.17
Manganese10	.124	.078	.075
Sulphur052	.080	.10	.06
Barium050	.081	.093	.03
Chlorine048	.096	.063	.04-.025
Chromium037	.068	.034	.01
Carbon032	.051	.13	.22
Fluorine030	.030	.10	.04-.025
Zirconium026	.052	.017	.02-.01
Nickel020	.031	.020	.005
Strontium019	.034	.034	.005
Vanadium017	.041	.017	.00n
Cerium, yttrium ..	.015	.02000nn
Copper010	.010000,n
Uranium008	.000,00n000,00n
Tungsten005	.000,00n000,00n
Lithium004	.005	.004	.004
Zinc004	.004000,n
Columbium, tantalum	.003	.000,00n000,000n
Hafnium003
Thorium002	.000,00n000,000,n
Lead002	.002000,n
Cobalt001	.00300n
Boron001	.00100n
Glucinum001	.00100n
	100.000	100.000	100.000	100.000

¹ Taken from Clarke, F. W., and Washington, H. S. (U. S. Geol. Survey Professional Paper No. 127, 20, 1924). It shows the averages obtained by several workers in this field. The reader is referred to the sources cited in the reference for further details. The numbers at the head of the columns refer to authors cited by Clarke and Washington.

to the list of commonly used metals. It is useful by itself but is even more useful when alloyed with aluminum.

TABLE II.
Average Composition of Igneous Rocks.
Less common and rare elements.¹

	5	6	7
Cerium, yttrium	1.5×10^{-4}	2×10^{-4}	$n \times 10^{-6}$
Copper	1×10^{-4}	1×10^{-4}	$n \times 10^{-6}$
Uranium	8×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-8}$
Tungsten	5×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-8}$
Lithium	4×10^{-5}	4×10^{-5}	4×10^{-5}
Zinc	4×10^{-5}	4×10^{-5}	$n \times 10^{-5}$
Columbium, tantalum	3×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-9}$
Hafnium	3×10^{-5}
Thorium	2×10^{-5}	$n \times 10^{-8}$	$n \times 10^{-9}$
Lead	2×10^{-5}	2×10^{-8}	$n \times 10^{-8}$
Cobalt	1×10^{-5}	3×10^{-5}	$n \times 10^{-5}$
Boron	1×10^{-5}	1×10^{-5}	$n \times 10^{-5}$
Glucinum	1×10^{-5}	1×10^{-5}	$n \times 10^{-5}$
Molybdenum	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-7}$
Rubidium	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Arsenic	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Tin	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Bromine	$n \times 10^{-6}$	$n \times 10^{-6}$	$n \times 10^{-5}$
Caesium	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-8}$
Scandium	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-12}$
Antimony	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-5}$
Cadmium	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-5}$
Mercury	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-5}$
Iodine	$n \times 10^{-7}$	$n \times 10^{-7}$	$n \times 10^{-5}$
Bismuth	$n \times 10^{-8}$	$n \times 10^{-8}$	$n \times 10^{-9}$
Silver	$n \times 10^{-8}$	$n \times 10^{-8}$	$n \times 10^{-9}$
Selenium	$n \times 10^{-8}$	$n \times 10^{-8}$	$n \times 10^{-9}$
Platinum	$n \times 10^{-9}$	$n \times 10^{-9}$	$n \times 10^{-10}$
Tellurium	$n \times 10^{-9}$	$n \times 10^{-9}$	$n \times 10^{-10}$
Gold	$n \times 10^{-9}$	$n \times 10^{-9}$	$n \times 10^{-10}$
Iridium	$n \times 10^{-10}$
Osmium	$n \times 10^{-10}$
Indium	$n \times 10^{-11}$	$n \times 10^{-11}$	$n \times 10^{-11}$
Gallium	$n \times 10^{-11}$	$n \times 10^{-11}$	$n \times 10^{-11}$
Thallium	$n \times 10^{-10}$	$n \times 10^{-10}$	$n \times 10^{-11}$
Rhodium	$n \times 10^{-11}$
Palladium	$n \times 10^{-11}$
Ruthenium	$n \times 10^{-11}$
Germanium	$n \times 10^{-11}$	$n \times 10^{-12}$	$n \times 10^{-12}$
Radium	$n \times 10^{-12}$	$n \times 10^{-14}$	

¹ Taken from Clarke, F. W., and Washington, H. S. (U. S. Geol. Survey Professional Paper No. 127, 21, 1924). The numbers at the head of the columns refer to authors cited by Clarke and Washington. The authors obviously consider these values as orders of magnitude. It is quite possible that these figures will have to be changed when more accurate data are obtained, but it is doubtful if the changes will significantly alter these orders of magnitude.

Table I shows that the three elements iron, aluminum, and magnesium are among the most abundant elements. We have learned to use, either by themselves or as alloys, a host of metallic elements that are present in the Earth in minor or even very low concentrations. Many of them, on the basis of our chemical and physical knowledge of their properties, are rated as common elements. Surely copper, silver, gold, the platinum metals, lead, zinc, mercury, bismuth, manganese, titanium, nickel, and chromium are familiar elements, yet as compared with iron, aluminum, and magnesium they are, with respect to the Earth's crust, uncommon. They are used either alone or in alloys; the alloys of nickel and chromium with iron have enormously increased the usefulness of this common element. It can be truly said that we are living in an age of alloys.

We are not concerned with the metals only, for many of the elements are most useful to man when they are combined with the two most abundant elements, namely, silicon and oxygen; the enormous development of the ceramic industries is a case in point.

This age is also becoming increasingly more dependent on substances that exercise a controlling influence on both chemical and physical processes. Catalysis and electron emission have assumed an importance that is out of all proportion to the amount of material used. In the constant endeavor to find materials that will increase catalytic action and electron emission and that will increase the usefulness of our commonly employed elements, it is quite natural that more attention will be given not only to the common and abundant ones but also the rare and less familiar ones.

In this paper an element will be considered as rare when its concentration in the Earth's crust¹ falls below 0.01 per cent, as shown in Tables I and II. When we consider the mass of the lithosphere (19×10^{18} metric tons),² the total amount of any of these is enormous, but this capacity factor is of little use if the cost of extraction is not commensurate with the market value of the product. It is true that gold, one of the rarest of elements, can be extracted economically from rather lean materials, but if all countries were to abandon the gold standard there would be but little gold extracted. Radium, in spite of its great value and usefulness, would remain a fas-

¹ Washington, H. S.: *J. Franklin Inst.*, 190, 757, 1920.

² Clarke, F. W., and Washington, H. S.: *U. S. Geol. Survey Professional Paper No. 127*, 17, 1924.

cinating chemical curiosity but for the fact that it has been concentrated in uranium ores which in themselves represent a concentration from leaner material. The elements beryllium, molybdenum, vanadium, tungsten, thorium, the "rare earths," tantalum, and surely radium, are very rare elements but our chemical and physical knowledge of their properties has increased to such an extent that they are less familiar only to those who do not have occasion to work with them; they are now extensively employed in the industries. It is quite possible that cesium, rubidium, columbium, thallium, gallium, and even rhenium, will soon be in the same category of useful elements.

None of the rare elements are likely to be useful unless we find them concentrated in nature to such an extent that they can be economically extracted with respect to market conditions. It is opportune, therefore, to review our knowledge, scanty though it may be, of the probable methods of concentration by natural processes.

Igneous rocks constitute 95 per cent of the crust of the Earth.³ They are the source of the shales, sandstones, limestones, and soil that make up the remaining 5 per cent. It is obvious, therefore, that they must also be the source of all known elements. The geochemistry of the various elements considers their distribution throughout the Earth. Since we have factual knowledge of only 3 per cent of its radius⁴ our information concerning the more deeply seated portions must be by analogy with the meteorites or by inference from the data derived from seismological studies.⁵

Although it is true that the discussion of the distribution of the rare elements deep within the Earth and in meteorites does not come within the scope of this discussion, a brief review of the findings of Ida and Walter Noddack⁶ will be worth while. They have made analyses of the rare elements in meteorites, in extremely scarce rocks of deep-seated origin, in igneous rocks, and in sedimentary rocks. Their analyses indicate the same low concentrations recorded in Tables I and II. It is not at all unlikely, therefore, that most of the concentrations remain low throughout the stages of differentiation

³ Clarke, F. W., and Washington, H. S.: *Op. cit.*, p. 2.

⁴ Niggli, P.: *Das Magma und seine Produkte*, Akademische Verlagsgesellschaft, Leipzig, 1937.

⁵ Adams, L. H.: *Sci. Monthly*, 44, 199, 1937.

⁶ Noddack, Ida, and Noddack, Walter: *Z. physik. Chem.* A154, 207, 1931.

indicated below on account of the scarcity of the elements. Every analyst will appreciate the difficulty of removing a slight trace of some impurity which persists no matter how many operations he may use to remove it through concentration, either as a precipitate or by solution. It has been said that the best analysis is only an asymptotic approach to perfection.⁷ The research worker in seeking for the rare elements must therefore resort to the keenest of analytical tools such as optical and X-ray spectroscopy and must often combine them with chemical methods that permit coprecipitation of the rare with more readily removed elements. Given sufficient material and sensitive methods of analysis it is quite probable that all elements can be determined in any rock, but it is far more important to know how they have been concentrated in nature.⁸

Geologists are now in fair agreement that such igneous rocks as are now amenable to investigation have in a great measure been derived from a homogeneous igneous mass by a process of differentiation. The theory of petrographical provinces⁹ indicates that this homogeneous mass may have had a uniform bulk composition, nevertheless it gave birth to rock sequences that differed with respect to mineral species in different parts of the original mass. It is well to bear in mind, however, that while it is true that differentiation has taken place in many localities, there are huge igneous masses called batholiths that have been intruded under the crust of the Earth and have crystallized and cooled without differentiation.¹⁰ Much remains to be done to give us a clearer view of these processes, but even though our knowledge concerning the nature of the materials below the Earth's crust is limited, considerations based on the study of seismic phenomena, elasticity of rocks,¹¹ and phase rule studies^{12, 13} of the rocks that have been brought to the surface have produced theories which in spite of the fact that they must later be either amplified or discarded altogether are helpful in giving us a picture of what is probably going on.

⁷ Annual Survey of American Chemistry, 5, 108, 1930.

⁸ Lindgren, W.: *Econ. Geol.*, 18, 419, 1923.

⁹ Harker, Alfred: *The Natural History of Rocks*, The Macmillan Co., New York, p. 88, 1909.

¹⁰ Lindgren, W.: *Mineral Deposits*, McGraw-Hill Book Co., New York, p. 111, 1933.

¹¹ Adams, L. H., and Williamson, E. D.: *Smithsonian Inst. Repts.*, p. 241, 1923.

¹² Bowen, N. L.: *This Journal*, 39, 175, 1915; *The Evolution of the Igneous Rocks*, Princeton University Press, Princeton, 1928.

¹³ Niggli, P.: *Op. cit.*, p. 36.

On the basis of the known density of the Earth taken as a whole, about 5.5, and the density, 2.8, of the known granitic shell which makes up the bulk of the Earth's crust, it naturally follows that the Earth's core must contain material of higher density. On the basis of analogy with the composition of meteorites it is assumed that the core is composed of the two metals nickel and iron. The study of seismic phenomena, the known compressibility of rocks and their elastic properties, and the analyses of igneous rocks all indicate that there are three principal shells covering the core. The bulk composition of the layer next to the core corresponds to that of a peridotite, the next shell to that of a basalt, and the surface layer to that of a granite. The statistical studies of Clarke and Washington¹⁴ confirm this theory with respect to the surface shell for they show that in spite of the many different kinds of igneous rocks, the bulk composition corresponds to that of a granite. It is possible that the basaltic shell with its relatively low silica content grades into the siliceous granite.

Geologists believe that rocks of low silica content such as eclogites and peridotites are of deep-seated origin; the physicist has found from his studies that the known rocks that would account for the observed sudden increase in velocity of seismic waves are just these eclogites and peridotites.

The granitic shell is believed to be about 60 kilometers thick and somewhat unevenly distributed. It is thickest in the continental masses and thins out to almost nothing in the great oceanic deeps. The average analysis of the rocks of the Earth's crust certainly points to a granitic composition, but the intrusion into the shell and extrusion on the surface by igneous activity of rocks of different composition varying from a basalt to a rhyolite show clearly that a process of differentiation has taken place. The depth¹⁵ at which these changes took place is at present a matter of conjecture, but it quite probably happened below the granitic shell. Our knowledge concerning the distribution of the rare or less familiar elements has been derived, of course, from the layer whose average composition is a granite. Yet the very fact that differentiation has taken place is a matter of considerable interest, for in this manner minerals of economic importance have been concentrated.¹⁶

¹⁴ Clarke, F. W., and Washington, H. S.: *Op. cit.*, p. 8.

¹⁵ Daly, Reginald A.: *Igneous Rocks and the Depths of the Earth*, McGraw-Hill Book Co., New York, 1933.

¹⁶ Vogt, J. H. L.: *Econ. Geol.*, 21, 207, 1926.

Poulett Scrope¹⁷ was one of the earliest investigators to promulgate the idea that a huge mass of heated igneous material under the surface of the Earth could differentiate. "It is quite conceivable that, when exposed in the focus of a volcano to successive liquefaction and reconsolidation, the heavier minerals may sink by a sort of filtration through the lighter ones, the upper portions of the mass becoming consequently more felspathic, the lower more ferruginous or augitic." This beautifully simple theory was bitterly opposed by many geologists but the entire problem was once more taken up in the light of the advances made in geology and physical chemistry by M. Schweig.¹⁸ Relatively little attention was paid even now to this newer presentation of differentiation. About ten years later, the work of N. L. Bowen¹⁹ truly aroused the interest of the geologists in this problem. By this time, however, the experimental side of petrography received such decided support from phase rule considerations and from the new experimental technique developed at the Geophysical Laboratory of the Carnegie Institution, that Bowen could with much greater assurance point out to the geologist that fractional crystallization in a large body of molten magma can take place. Objections²⁰ have been raised to parts of Bowen's theory, nevertheless the definite possibility and probability of such differentiation have been demonstrated.

In this brief résumé of differentiation mention has been made only of siliceous rocks. It is well at this point to call attention to the work of J. H. L. Vogt²¹ and of V. M. Goldschmidt,²² who consider it possible that some basic magmas have become so greatly enriched in sulphur that sulphides of the heavy metals, particularly sulphides of iron and nickel, may have separated on cooling. Goldschmidt postulates that an original fluid globe separated on cooling into three immiscible layers: at the core a metallic melt, which grades into one in which the sulphides dominate, and this in turn grades into a siliceous shell containing a gas phase—the atmosphere. It is believed by some

¹⁷ Scrope, G. Poulett: *Volcanos*, Longmans-Green and Co., London, p. 125, 1862.

¹⁸ Schweig, M.: *Neues Jahrb. Mineral. Geol., Beilage*, Bd. 17, 516, 1903.

¹⁹ Bowen, N. L.: *The Evolution of the Igneous Rocks*, op. cit.

²⁰ Fenner, C. N.: *Bull. Geol. Soc. Am.*, 49, 367, 1938.

²¹ Vogt, J. H. L.: *Die Sulfid Silikat Schmelzlösung*, Jacob Dybwad, Kristiana, 1919.

²² Goldschmidt, V. M.: *Videnskaps.-Skrifter I, Mat.-naturv. Klasse No. 3*, 1923.

geologists that the well-known platinum-rich copper nickel sulphide ore bodies of Sudbury have resulted from a process of differentiation through fractional crystallization, but there is as yet no unanimity of opinion on this point. The sulphide ores are, however, associated with a huge mass of intruded igneous rocks, and it is believed that magmatic differentiation played an important rôle in their origin. This also seems to apply to the segregation of the platinum metals in many basic rocks of the Ural Mountains in Russia, Columbia, California, and South Africa, and to the segregation of chromite, magnetite, and the titanium-iron mineral ilmenite,²³ but even here the influence of post-magmatic effects of aqueous solutions and volatile constituents is not denied.

Considerable impetus has recently been given to the elucidation of the theory of segregation and concentration of the sulphides by Merwin and Lombard.²⁴ This is the first attempt to apply phase rule principles to these vaguely understood processes. The three-component system, copper, iron, and sulphur, was studied at various temperatures and at a definite vapor pressure of sulphur. The region of stability of the iron sulphides, copper sulphides, copper-iron sulphides, and of a series of solid solutions of the various sulphides was thereupon determined.

As differentiation progresses in the more acidic portions of the large igneous masses that have been considered in this review, the volatile constituents such as water, HCl, HF, H₂S, CO₂ that were present in solution begin to assert themselves by virtue of their becoming more concentrated. It is now well established that water to the extent of about 1 or 2 per cent can lower the fusion of difficultly fusible rocks such as a granite by over 300°. Morey²⁵ and Goranson²⁶ have shown that as crystallization and cooling in a closed system continue, the volatile constituents, especially water, can generate enormous pressures on the constraining mantle. If the mantle is not strong enough to withstand the pressure it will be ruptured, and igneous materials, including the gases, will be ejected through volcanic activity. It is also possible that the constraining mantle may be strong enough to withstand rupturing, but

²³ Lindgren, W.: See ref. 10, p. 772.

²⁴ Merwin, H. E., and Lombard, R. H.: *Econ. Geol.*, 32, 203, 1937.

²⁵ Morey, G. W.: *J. Geol.*, 32, 291, 1924.

²⁶ Goranson, R. W.: *This Journal*, 22, 481, 1931; 23, 227, 1932; *Trans. Am. Geophys. Union*, 17, 257, 1936.

the boiler pressure, so to speak, is great enough to permit the injection of the siliceous mass of material into weaker layers of the mantle. It is by some such mechanism as this, together with probable chemical activity on the surrounding rock, that it is believed the end products of differentiation, namely, the pegmatite dikes,²⁷ are formed. These masses of material injected under high gas pressure are the happy hunting ground for those in search of rare elements.²⁸ Many of these elements have reached such a high degree of concentration that when combined with other elements they crystallize as distinct mineral species. The boron-bearing minerals, the rare earths, the cesium mineral pollucite, the lithium and cesium-rubidium-bearing micas, the fluo-borates, the fluorides, and the beryllium minerals are examples. They also contain many minerals such as molybdenite within which have been concentrated some of the extremely rare elements of which rhenium is an example. We have now reached a stage in the differentiation in which volatile constituents, especially water, play an important rôle. It was said above that there are relatively few sulphide deposits whose origin by magmatic segregation is unambiguous. The reason is that near the end of the various processes of differentiation water and other volatile constituents such as CO₂, HCl, HF, B, and H₂S, at temperatures which we know from field and laboratory evidence may be as high as 650°, accumulate and produce an intensely chemically active environment. Very little of a fundamental nature is known of this complicated system. At present it can not be studied as an entirety and must be broken down into a simpler form. This has been done for part of the system, Fe-Cl-H₂O, by Stirnemann.²⁹ Similar fundamental studies of vapor phase activity are now being carried out by G. W. Morey and his coworkers.³⁰ The problem, by virtue of the intense chemical activity of its components, is extremely difficult, but at least an attempt must be made to obtain its solution if we wish to coordinate field evidence with laboratory investigation.

The term "water" was applied to one of the constituents in the igneous materials, but it is perhaps best to give it its usual

²⁷ Lindgren, W.: Ref. 10, p. 118.

²⁸ Goldschmidt, V. M.: Nachr. Ges. Wiss. Göttingen Math.-physik. Klasse, p. 370, 1930.

²⁹ Stirnemann, E.: Neues Jahrb. Mineral. Geol., Beilage Bd., A52, 334, 1935; A53, 59, 1926.

³⁰ Morey, G. W.: Work in progress.

designation of H_2O , for in the environment just mentioned it is above its critical temperature and the properties of liquid and vapor become indistinguishable. As cooling takes place it will exist in both phases, and all the active chemicals referred to may be either in solution or in the vapor phase. Naturally the intensity of the chemical activity will depend on temperature and percentage concentration. This point will be discussed again later in this review. It must be obvious from what has been said that the record of any magmatic segregation of constituents that may have taken place can be destroyed in its entirety by the chemically active gases that are produced in the last stages of differentiation. It is not amiss to call attention to the fact that "geological field research deals with end phenomena of completed reactions but with a very imperfect record of the earlier steps in the earth-making process."²¹

On page 393 the condition was postulated that the pressure of the vapor phase generated on crystallization of the silicate magma may reach such proportions that rupturing of the constraining mantle may take place. We thus have in its simplest form the beginning of volcanic activity which is, therefore, the surface manifestation of more deep-seated activity. We no longer have a completely closed system, and all the changes brought about by change in pressure and lowering of temperature will take place. The phenomena are not necessarily confined to the surface, for the hearth of the volcano may still be several miles below the orifice; nevertheless the physical-chemical environment is that of an essentially open system in which chemical changes may take place quite rapidly.

We have reached a stage in the history of an igneous body which is more or less amenable to direct study. Volcanic phenomena have been observed for a long period of time and naturally more attention has been given to the description of types of solid materials, the dust clouds, the lava, and the fragmental material which contribute to the construction of the volcanic edifice. Some of the earlier writers on volcanic activity realized that the extrusion of solid materials certainly accounts for the bulk of the material brought to the surface, but they also recognized the fact that at many volcanoes vapors, especially water, played a very important part in providing the

²¹ Day, A. L., Allen, E. T., and Iddings, J. P.: Carnegie Inst. Wash., Pub. No. 1, 17, 1905.

mechanism by which the solid materials were brought to the surface.^{82, 83}

In the course of the early part of this century attention was directed specifically to these vapors and to the minerals which were formed by the interaction of the vapors with the constituents in the extruded rocks. The story is not quite so simple as just stated. The rock materials that are brought to the surface are not necessarily composed of the minerals and constituents in the last stages of differentiation. Interaction with the constraining mantle may take place in the hearth of the volcano and introduce material which may have quite a different composition. Then, too, interaction of the chemical vapors with this material may bring about a sequence of changes quite different from those peculiar to the unaltered segregation. The possibility, however, exists of coordinating field studies in nature's laboratory at volcanoes with fundamental studies carried out under carefully controlled conditions.

The volcanic eruption that took place in 1912 in the Valley of Ten Thousand Smokes^{84, 85} located on the Alaskan Peninsula offered an unusual opportunity for studying the chemical aspects of the later stages of igneous activity. The activity in the Valley was, according to Fenner,⁸⁶ brought about by the injection of the very siliceous lava, rhyolite, under the old Valley floor. The pressure exerted by the volatile constituents was sufficient to rupture the floor and permit the igneous materials to reach the surface. The lava was highly charged with volatiles which on sudden relief of pressure escaped into the atmosphere and deposited a great mass of hot and very porous glassy pumice. The Valley is roughly four miles wide and twelve miles long and it is estimated that a cubic mile of material was extruded. Thousands of fumaroles (steam vents) were situated in this rhyolitic pumice, and in 1919, seven years after the eruption, were quite active both thermally and chemically. Steam temperatures as high as 640° C were found, indicating that the temperature of the more deeply buried material was still high. Allen and Zies⁸⁷ collected and analyzed the

⁸² Niggli, P.: *Op. cit.*, Introduction.

⁸³ Scrope, G. Poulett: *Op. cit.*, p. 125.

⁸⁴ Allen, E. T., and Zies, E. G.: *Nat. Geogr. Soc., Contrib. Tech. Papers, Katmai series No. 2*, 75, 1923.

⁸⁵ Zies, E. G.: *Nat. Geogr. Soc., Contrib. Tech. Papers, Katmai series No. 3*, 159, 1924, and *No. 4*, 1, 1929.

⁸⁶ Fenner, C. N.: *J. Geol.*, 28, 569, 1920.

⁸⁷ Allen, E. T., and Zies, E. G.: *Op. cit.*

fumarole gases and found that they contained about 99.5 per cent of water, 0.2 per cent of gases insoluble in water, and a total of 0.3 per cent of the acid gases, HCl, HF, and H₂S. The bulk of the gas is obviously steam, but we must not be misled by the low concentration of the other gases. An estimate³⁸ was made of the total amount of gases that would be emitted if the rate observed in 1919 were to continue. This is only an estimate, to be sure, but reasons have been given in the references cited for believing that it is of the right order of magnitude. It is seen from Table III that even though the

TABLE III.

Amount of Acid Gases Emitted by the Fumaroles in the Valley of Ten Thousand Smokes in 1919. Zies.¹

Estimated volume of steam calculated at 100°, 760 mm. = 26×10^6 liters per second.

Per cent	Steam contained kg. per sec.	Metric tons per year
0.117 HCl	36.0	1.3×10^6
0.032 HF	5.6	0.2×10^6
0.029 H ₂ S	8.4	0.3×10^6

¹ Zies, E. G.: Nat. Geogr. Soc. Contrib. Tech. Papers, Katmai series, No. 4, p. 4, 1929.

percentage concentration of the dominant acid constituents is small, yet the total amount from this single volcanic area is enormous. It is essential, therefore, in dealing with these natural phenomena to keep both the intensity and the capacity factors clearly in mind.

The presence of large total amounts of fluorine is particularly noteworthy, for it is one of the most active of the acid gases in decomposing silicates. The interaction of the acid gases with the extruded pumice decomposed the latter and set free a host of halides, sulphides, and oxides whose presence in the pumice was not even surmised. The reader is referred to the original articles³⁹ for the detailed account of the investigations. It will suffice for our present purpose to call attention to a few items of geochemical importance. Interest was first directed to the concentration of minor elements when barium was found in the incrustations around the vents in

³⁸ Zies, E. G.: Nat. Geogr. Soc., Contrib. Tech. Papers, Katmai series, No. 4, 1, 1929.

³⁹ Zies, E. G.: Ref. 35.

amounts that represented a hundredfold increase over that determined in the pumice itself. Magnetite (Fe_3O_4) was found in many of the vents, and although no reliable estimate could be made of the total amount, it was obvious that it must be thought of in terms of tons rather than a few pounds. The evidence is also clear that the magnetite was derived through a vapor phase activity and represents, therefore, the concentration of the iron derived from the more deeply seated portions of the pumiceous deposit. The magnetite was so beautifully crystallized that one might easily assume that we were dealing with a relatively pure material. The analysis in Table IV shows, however, that this was far from the truth.

TABLE IV.

Foreign Constituents in the Fumarolic Magnetite Found in the Valley of Ten Thousand Smokes. Zies.*

Weight of sample grams	Weight of substance as determined grams	Calculated as	Per cent
10	Hg	none
10	0.0007 PbO	Pb	0.005
10	Bi	none
10	0.0233 Cu	Cu	0.23
10	0.0054 MoO ₃	Mo	0.04
10	0.0005 SnO ₂	Sn	0.004 (approximate)
10	As	none
10	Sb	present [†]
10	Cr	none
10	V	none
10	colorimetrically	TiO ₂	0.005
10	0.0474 Zn	Zn	0.47
10	0.0005 NiC ₂ H ₄ N ₄ O ₄	Ni	0.01
10	0.0003 CoO	Co	0.02
1	colorimetrically	MnO	0.13
1	0.0196 BaSO ₄	S	0.27
20	0.0110 NaCl + KCl	NaCl	0.05
10	0.0530 siliceous residue		0.53
1	0.0005 Al ₂ O ₃ [‡]		

* Zies, E. G.: Nat. Geogr. Soc., Contrib. Tech. Papers, Katmai series No. 4, p. 6, 1929.

[†] Definitely identified spectroscopically and not present in the blank.

[‡] Present in portion of fumarolic magnetite soluble in HCl and indicates that alumina was not present as part of magnetite molecule.

When it was found that a well crystallized mineral such as magnetite could contain so many extraneous minor elements, it was decided to subject the other incrustations that had been

collected to detailed chemical and spectrographic analysis. It was then discovered that many elements were present other than those found in the magnetite. Thus bismuth, gallium, thallium, boron, germanium, arsenic, selenium, and tellurium were definitely proved to be present. Molybdenum was found not only in the magnetite but in the other incrustations as well, often in the form of the hydrated oxide molybdenum blue. The concentration of this compound was great enough to color areas covering half an acre.

The pumiceous material in its purest form was next subjected to the same analytical procedure and every element found in the incrustations was shown to be present in the pumice. The concentration in the incrustations was almost one hundred times that in the pumice. Practically all the elements mentioned above have one characteristic in common; namely, their halides and, in some cases, their sulphides and oxides are volatile at the temperatures prevailing in the Valley of Ten Thousand Smokes. We obviously have here a mechanism by which large amounts of elements present in traces in the igneous materials can be concentrated at or near the surface and brought up from more deeply buried materials. The condition is here met that in order to bring about this type of concentration there must be a constant shifting of equilibrium due to lowering of the pressure and temperature. Niggli⁴⁰ has given considerable thought to the volatile products of igneous materials and has clearly presented the theories underlying the probable changes that take place on the cooling of a magma. It will repay those interested in this phenomenon to study his presentation carefully.

In a sense this period of expulsion of volatile constituents is the last stage of what may be called true igneous activity, but it is by no means the last chapter in the study of concentration of the elements. One illustration will suffice. In 1923, C. N. Fenner continued his studies in the Valley of Ten Thousand Smokes and at our request made an effort to collect more of the magnetite found in 1919, but none was found. The temperatures had fallen to a point where active condensation of the steam was taking place; the acid gases were now in solution, and the magnetite was decomposed. The influence of hydrogen sulphide was now apparent, for in the new chemical environment only such compounds could persist as

⁴⁰ Niggli, P.: *Op. cit.*

are relatively insoluble in acid. In place of magnetite, such minerals as covellite (CuS), chalcocite (Cu_2S), and sphalerite (ZnS) were found. These represent a further concentration of the copper and zinc. This illustration is cited to show the complex mechanism by which concentration is brought about.

These are in brief the methods by which concentration of the elements may be attained in nature. We have seen, however, that many of the rare and less familiar elements are present in igneous materials in such extremely low concentrations that it is possible for them to be dragged along as persistent impurities, so to speak, throughout the process of rock differentiation. It would seem almost futile to hope to find them in the rocks in any concentration of economic importance, no matter how valuable their chemical or physical properties may be. The case is not so hopeless, however, as it may seem.

In the discussion of the formation of the pegmatite dikes it was stated that some of the rare elements may be too dilute to form a definite mineral, yet may be trapped by other minerals. Every analyst is familiar with a related process. For instance, extremely minute amounts of fluorine can be carried out of a neutral solution if barium is added and subsequently precipitated as barium sulphate. Gallium often escapes detection when present in low concentrations, but it can be concentrated by hydrogen sulphide if zinc is present. This phenomenon of coprecipitation is but little understood, but in the writer's opinion it is an important agency in concentrating some of the rare elements. There is still another mechanism by which minerals can gather up elements that exist in solution at low concentration. The magnetite found in the Valley of Ten Thousand Smokes contained appreciable amounts of manganese and zinc within the magnetite itself. This reminds one of the important mineral group called the spinels, of which magnetite and the zinc- and manganese-bearing franklinite are examples. Still another example: the cesium, rubidium, and gallium often found in lepidolite, one of the many minerals found in pegmatite dikes, can be fairly easily concentrated in the alums that are readily obtained after the mica is decomposed.

H. B. Grimm⁴¹ has shown that the ability to form such mixed crystals depends on the dimensions of similarly constructed crystal species and also on the dimensions of the sub-

⁴¹ Grimm, H. B., and Wagner, G.: *Z. physik. Chem.*, 132, 131, 1928.

stituted atom species. V. M. Goldschmidt, a most indefatigable worker on the problem of the distribution of the elements, has in a series of articles called attention to the high degree of probability that the segregation of the elements in crystals is governed by the relation between crystal structure and the dimensions of the atom and ion species. If this is true, then in the course of the crystallization of the various mineral species all extraneous elements whose atomic or ionic dimensions are either too small or too large to be taken up by the crystals are concentrated in the mother liquor. Perhaps the finest contribution made by V. M. Goldschmidt⁴² is his determination of the ionic radii of many of the elements in Ångström units. The values of the radii are based on X-ray studies of crystal structure, which furnish the so-called lattice dimensions, and on the determinations by J. A. Wasastjerna⁴³ of the ionic dimensions of F^- and O^{2-} . The assumption is also made that in general the anion-cation distances of closest approach should be given by the sum of the corresponding radii. X-ray studies of a large number of combinations of the elements with oxygen, fluorine, and sulphur were made by Goldschmidt in order to obtain a basis for his calculations. Pauling also calculated the ionic distance from quite different data and obtained results that agree well with those of Goldschmidt. These results are tabulated in the "International Tables for the Determination of Crystal Structure." They apply to distinct crystal groups, and due regard must be given to the structure type, valency, and coordination number. The interested reader is referred to the citations for the necessary details. These ionic and atomic dimensions provide us with a powerful tool for following the probable course of the segregation of the elements that exist in minor concentration in the rocks and have enabled V. M. Goldschmidt⁴⁴ to make several trenchant observations. The lattice dimensions of similar aluminum and gallium compounds are shown in Table V. This striking similarity in dimensions is also reflected in the similarity of the ionic radii.

⁴² Goldschmidt, V. M.: *Geochemische Verteilungsgesetze der Elemente* VIII. Skrifter Norske Videnskaps-Akad. i Oslo, I, Mat.-Naturv. Klasse, 1926, No. 8, 7, 1927.

⁴³ *International Tables for the Determination of Crystal Structure*, Vol. 2, Gebrüder Bornträger, Berlin, 1935.

⁴⁴ Goldschmidt, V. M.: *Geol. Fören. Förh.*, 56, 385, 1934.

TABLE V.
Lattice Dimensions of Similar Compounds of Aluminum and Gallium.¹

Al compounds	Å	Å	Ga compounds
Al ₂ O ₃	5.13	5.28	Ga ₂ O ₃
LaAlO ₃	3.78	3.89	LaGaO ₃
AP	5.451	5.436	GaP
AlAs	5.628	5.635	GaAs
AlSb	6.091	6.093	GaSb

¹ Taken from V. M. Goldschmidt: *Naturwissenschaften*, 18, 1003, 1930.

In Table VI are shown the ionic radii of a few elements of equal valency. They are arranged in groups of similar dimensions, and a common element is associated with an element

TABLE VI.
Similarity in Ionic Radii of Rare Elements of Equal Valency Camouflaged by the Common Elements.¹

Å	Å	Å	Å	Å
Mg 0.78	Si 1.27	Al 0.57	Si 0.39	Zr 0.87
Ni 0.78	Pb 1.32	Ga 0.63	Ge 0.44	Hf 0.86

¹ Taken from V. M. Goldschmidt: *Naturwissenschaften* 18, 1003, 1930.

whose average concentration in the Earth's crust is low. They have been selected for this presentation because this same association is repeatedly found in nature.

The same striking similarity in ionic radii obtains for the trivalent yttrium series of elements, as shown in Table VII. The analyst finds it extremely troublesome to separate these

TABLE VII.
Similarity in Ionic Radii of the Yttrium Elements.¹

Å	Å	Å
Gd 1.11		Ho 1.05
Tb 1.09	Y 1.06	Er 1.04
Dy 1.07		Yb 1.00
		Cp 0.99

¹ Taken from V. M. Goldschmidt: *Naturwissenschaften* 18, 1004, 1930.

elements, and Nature has had the same difficulty. The average percentage concentration of these elements in the Earth's crust is extremely low; they are not removed by the usual processes of differentiation and therefore concentrate in the mother liquor—the pegmatites. Many other examples could be cited, but for our purpose the above will suffice.

V. M. Goldschmidt⁴⁵ has given the name "Tarnung" or "camouflage" to this tendency for the rare elements to be associated with and obscured by some more common element whose concentration in the siliceous igneous fluids is high enough to form a distinct mineral. He has also shown that extraneous elements whose valencies differ but whose ionic radii are similar may also be concealed or camouflaged within some common mineral. Table VIII contains several examples for both the common and rare elements.

TABLE VIII.
Similarity in Ionic Radii of Elements Differing in Valency
Camouflaged by the Common Elements.¹

	A	Valency		A	Valency
Li	0.78	1	Ca	1.06	2
Mg	0.78	2	Y	1.06	3
Na	0.98	1	Sc	0.83	3
Ca	1.06	2	Zr	0.87	4
K	1.33	1	Ti	0.64	4
Ba	1.43	2	Nb	0.69	5

¹ Taken from V. M. Goldschmidt: *Naturwissenschaften* 18, 1004, 1930.

Many years ago H. S. Washington⁴⁶ called attention to the fact that calcium is frequently found with sodium in the soda feldspars, and barium with the potassium feldspars. V. M. Goldschmidt's work, based on X-ray studies of crystal structure and X-ray analysis, now provides an explanation for the association of the elements referred to, and has thereby given great impetus to the study of their geochemistry.

The geochemical cycle of germanium as worked out by Goldschmidt and Peters⁴⁷ is of unusual interest. The former, on the basis of similarity in dimensions of ionic radii had indicated that this element should be associated with silicon in the silicates. Papish⁴⁸ by means of his spectrographic analyses showed that germanium is in fact widely distributed in silicate minerals. Goldschmidt and Peters⁴⁹ showed that germanium could probably be absorbed by the roots of plants. They found, for instance, 1.6 per cent of GeO_2 in the ashes derived from

⁴⁵ Goldschmidt, V. M.: See ref. 44.

⁴⁶ Washington, H. S.: *Trans. Am. Inst. Mining Eng.*, 1908.

⁴⁷ Goldschmidt, V. M., and Peters, Cl.: *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, p. 141, 1933.

⁴⁸ Papish, J.: *Econ. Geol.*, 24, 470, 1929.

⁴⁹ Goldschmidt, V. M., and Peters, Cl.: *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, p. 371, 1933; see also V. M. Goldschmidt: *Ind. Eng. Chem.*, 27, 1100, 1935.

some English coals, surely an extraordinary concentration of what is usually called a rare element.

The geochemistry of rhenium has been studied very thoroughly by its discoverers, Ida and Walter Noddack.⁵⁰ A truly enormous number of substances have been analyzed by them within a comparatively short time both by X-ray and by optical spectroscopy. No claim seems to be made by them for great accuracy of the determinations, nevertheless their work brings out clearly where this extremely rare element is likely to be found in nature. Here, again, similarity in ionic radii seems to be the guiding principle in showing that the greatest concentrations will be found in the molybdenites associated with pegmatitic minerals. Molybdenum and rhenium are much alike in their chemical properties and in the dimensions of their ionic radii. The work of Ida and Walter Noddack also brings out a point that has been frequently referred to, namely, the investigation of the by-products and so-called waste materials in the industries. Rhenium has been extracted from a molybdenum by-product in amounts that definitely take this element out of the category of a chemical curiosity.⁵¹

Even though the useful elements found in ore bodies were derived from igneous materials through the processes of differentiation referred to in this review, yet their present concentration has in most cases been obtained through a complicated process of decomposition of the original materials and their reconcentration from solution in a favorable physical-chemical environment. The rare elements camouflaged in some mineral may also be reconcentrated when this mineral is decomposed through subsequent geochemical alteration.

It would behoove those who are interested in searching for the rare elements that are not found as distinct mineral species to sharpen their quantitative physical and chemical analytical tools and search for these less familiar elements in the minerals and waste products within which the guiding principle of similarity in ionic radii has shown they may be concealed. It will also be desirable to take cognizance of the chemical principles referred to in the discussion of the concentration of the elements in volcanic areas through vapor phase activity and through the solvent action of acid or even alkaline waters.

⁵⁰ Noddack, Ida, and Noddack, Walter: See ref. 6.

⁵¹ Feit, W.: *Z. angew. Chem.*, 43, 459, 1930.